PROGRESS REPORT

OF THE

WESTERN MARKETING AND NUTRITION RESEARCH DIVISION

July 1, 1971

Agricultural Research Service
UNITED STATES DEPARTMENT OF AGRICULTURE

This progress report includes a summary of the current research of the Division and a report of progress made during the preceding year. It is primarily a tool for use of scientists and administrators in program coordination, development and evaluation; and for use of advisory committees in program review and development of recommendations for future research programs.

The report is not intended for publication and should not be referred to in literature citations. Copies are distributed only to members of Department staff, advisory committee members and others having a special interest in the development of public agricultural research programs.

This report also includes a selected list of publications issued between July 1, 1970, and June 30, 1971. Complete lists of publications and patents are published semi-annually. Copies are available on request to the Division's headquarters: Western Regional Research Laboratory, Berkeley, California 94710.

Issued January 1972

This publication reports research involving pesticides. It does not contain recommendations for their use, nor does it imply that the uses discussed here have been registered. All uses of pesticides must be registered by appropriate State and/or Federal agencies before they can be recommended.

CAUTION: Pesticides can be injurious to humans, domestic animals, desirable plants, and fish or other wildlife -- if they are not handled or applied properly. Use all pesticides selectively and carefully. Follow recommended practices for the disposal of surplus pesticides and pesticide containers.

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INTRODUCTION

This report summarizes the current program and progress during FY 1971 on research conducted at the Western Marketing and Nutrition Research Division, Agricultural Research Service.

Research Areas Covered by this Report

The following research problem areas are within the scope of the Western Marketing and Nutrition Research Division: (1) new and improved fruit and vegetable products; (2) new and improved food products from field crops; (3) new and improved feed and industrial products from field crops; (4) new and improved poultry meat and egg products; (5) new and improved products from wool and mohair; (6) expansion of foreign markets for U.S. farm products; (7) protection of food supplies from harmful microorganisms and naturally occurring toxins; (8) alleviating soil, water, and air pollution; (9) insure food products free from toxic residues from agricultural sources; and (10) evaluating and improving the nutrient content of foods.

The farm commodities dealt with in this report are the cereal grains, wheat, rice, and barley; alfalfa and other forage crops; wool and mohair; citrus, subtropical, deciduous and other fruits; tree nuts; potatoes, dry beans and peas, and other vegetables; castor, safflower, sesame and other western oilseeds; and turkey and eggs. (Some phases of research on certain of these commodities are pursued in other Marketing and Nutrition Research Divisions.)

Pharmacological research for four Marketing and Nutrition Research Divisions is conducted at the Albany laboratory of the Western Division, and is described in the report as it applies to various subject areas.

Organization of the Division

The Western Marketing and Nutrition Research Division is one of five such Divisions of the Agricultural Research Service. Research and development are carried on for the Western Division by a staff headquartered in the Western Regional Research Laboratory, Berkeley, California. A smaller Department-owned laboratory is operated in Pasadena, California. Laboratory space and facilities in Puyallup, Washington, are utilized through a cooperative arrangement with Washington State University, Institute of Agricultural Sciences; and laboratory space and facilities in Honolulu, through a cooperative arrangement with the University of Hawaii.

The Berkeley research staff is organized into six commodity-oriented Laboratories (Cereals, Field Crops, Fruit, Poultry Products, Vegetables, and Wool and Mohair) and four functional Laboratories (Pharmacology, Microbiology, Chemical Physics, and Engineering and Development). The staff at Pasadena is organized as the Subtropical Fruit Laboratory. The Western Regional Research Laboratory at Berkeley also houses the Division Director's staff, the staff required for Administrative support of the Division, and that responsible for Plant Management--that is, operation of the buildings, facilities, and grounds.

Division scientists and engineers not only conduct or supervise research in their own experimental facilities, but also greatly extend the scope and influence of their work by planning and supervising developmental activities carried on by cooperating private firms, processor organizations, or industry groups, and by arranging for research by well-qualified scientists elsewhere under research contracts and grants. In addition, certain grants of research funds are placed with investigators in foreign countries; the cost of these foreign research efforts on behalf of American agricultural interests is borne by Public Law 480 funds.

EXAMPLES OF RECENT RESEARCH ACCOMPLISHMENTS

Dry Caustic Peeling of Fruits and Vegetables. Department scientists have developed new processes for peeling fruits and vegetables which show great promise in reducing the water pollution resulting from processing these commodities. The dry caustic peeling process, developed earlier for use on white potatoes, has been modified for use on various fruits and vegetables. The new processes involve a brief treatment with caustic soda, followed by mechanical removal of the peel. The peel material is recovered in a form which can be used for feed, or disposed of by returning to the land. Conventional peeling methods produce high volumes of water waste, with very high BOD. Different fruits and vegetables require different peeling apparatus and procedures. Pilot-scale trials have been successful on pears, table beets, turnips, apricots, freestone peaches, and chili peppers. A Federal Water Quality Administration grant has been awarded to a North Carolina cannery to test the commercial feasibility of dry caustic peeling of sweetpotatoes. The first commercial scale peeler for fruit, handling 15 tons per hour, started operating on cling peaches in California in 1971. The dry caustic peeling methods offer economic advantages to processors, by permitting pollution abatement at very lost cost or even, as in the case with potatoes, at a profit.

Freeze-leaching Improves French-fried Potatoes. By a new USDA process, extremely variable raw potato material can be used to manufacture frozen or par-fried potato strips. This product has uniform good color and superior textural quality. The process reduces storage losses, eliminates the need for post-storage conditioning at warm temperatures, and makes

possible the use of potato varieties not previously suitable for these products. A surface freezing with food grade refrigerant, followed by leaching of solubles from surface cells, eliminates the excessive darkening of french-fried potatoes caused by storage-induced increase in reducing sugars. The surface treatment also restricts the absorption of cooking oil (reducing cost of manufacture and caloric content of products) and protects crispness of products so they do not become limp on the consumer's plate. The process has been successfully tested in the laboratory and on continuous prototype equipment in commercial food operations. Equipment of two manufacturers has been used, and one of the manufacturers is negotiating to construct full commercial scale equipment for a major producer of refrigerated, par-fried potatoes. Several producers of frozen french-fried potatoes have sought detailed information in anticipation of introducing this new process as soon as large-scale equipment is successfully operated.

Alfalfa Xanthophylls for Poultry Rations. The inclusion of approximately one million tons of dehydrated alfalfa meal in poultry rations, both in the United States and overseas, is largely dependent upon the poultry pigmenting xanthophylls in alfalfa. Department scientists utilizing pilot- and industrial-scale dehydrators determined the best conditions to preserve xanthophyll during alfalfa dehydration. They found that up to 60 percent of the valuable poultry pigmenting xanthophylls may be destroyed during conventional dehydration. These losses were correlated with meal moisture and drier outlet temperatures. Vitamin E and the essential amino acid lysine were also found to be lost under adverse drying conditions. The conditions for preserving the xanthophyll and other nutrients have been included in USDA publications which have been distributed to most members of the American Dehydrators Association, at their request. Improved analytical procedures have also been developed to analyze the alfalfa meals for both total and the pigmenting xanthophylls. USDA scientists have isolated and fed to poultry the principal xanthophylls of alfalfa. They determined that the epoxide-xanthophylls are non-pigmenters for poultry and they developed a procedure which excluded these compounds from analysis. The new analytical method is now in use and forms the basis of pricing alfalfa used for poultry rations. Such developments enable feed formulators to confidently evaluate the xanthophyll content of alfalfa meals and compute least-cost feed formulations.

Individual Quick Blanching (IQB) for Pollution Abatement and Improved Nutritional Quality of Canned and Frozen Vegetables. Blanching of vegetables for canning and freezing is, after peeling, the second greatest source of water pollution in this processing industry. In-plant trials, using a two-stage blanching process (IQB) developed by Department scientists show promise for reducing blancher effluent strength (BOD) up to 80% of that of conventional methods. Vegetables to be blanched are held on a moving belt in a single layer while exposed for a short time to steam. The pieces are then piled in a deep layer on a second belt passing through an insulated chamber, thus allowing time for the heat absorbed in the steam chamber to penetrate the pieces. The new system

greatly reduces the volume of excess water resulting from blanching, which in conventional blanching leaches soluble nutrients from the vegetables. A predrying step, when combined with IQB, results in a process which essentially eliminates all blancher effluent. Two 300-pound-per-hour continuous pilot blanching lines, operating in a frozen food plant in the northern San Joaquin Valley of California, and in a Wisconsin canning plant, have attracted widespread industrial interest. At least one equipment supplier is considering manufacturing blanching equipment incorporating the IQB concept.

Lysine-fortified Bulgur for Overseas Markets. Bulgur has advantages in overseas markets and particularly in food aid programs. These advantages stem from widespread familiarity with wheat as a basic food and the relative blandness, low fiber content, and resistance to insect attack after processing into bulgur. The low lysine content of wheat, however, limits the nutritional value of the protein. If other protein is not available to balance the amino acid composition, much of the potential value of the wheat protein is not realized. The feasibility of infusing lysine hydrochloride into wheat during the production of otherwise normal bulgur was shown in work by Department scientists. Because the protein quality is markedly improved by addition of only 0.1% lysine, this procedure offers a direct and inexpensive way to enhance the nutritional value of bulgur. Specifications for a rinse-resistant, lysine fortified bulgur were prepared. Reliable analytical procedures were developed to monitor the process and to inspect commercially prepared lots to insure that proper amounts of lysine had been added. Over 7 million pounds of lysine-fortified bulgur were used to help alleviate hunger and malnutrition in Nigeria in 1969 and 1970. Recent purchases have been even larger, amounting to 10.5 million pounds contracted in July 1971.

Enzymic Processing to Soften Dates. Cellulase enzymes can be introduced into tough dates by a combined vacuum infiltration-hydration process (or in some cases, by simply spraying) to supplement the natural ripening process. This makes it possible to enhance the quality and consumer acceptability of low grade raw material frequently obtained from mechanical harvesters. USDA scientists based this new process on research findings on the enzyme systems involved in the natural ripening of Deglet Noor dates. As mechanical harvesting of dates became an economic necessity, the proportion of immature, tough dates in need of quality improvement increased. The new process offers a good chance to recover value in this crop, and commercial testing of the method has begun.

Salt Recovery from Processing Brines by Submerged Combustion. Each year, the U.S. food pickling industry generates an estimated 100 million gallons of used brine in its salting operations. The disposal of this amount of saline liquid waste, without causing water pollution, has become a problem of increasing urgency to the industry. The corrosive nature of the sodium chloride salt in the brine, and the fact that the waste stream is a mixture of a non-biodegradable salt and organic solids, make the disposal problem a particularly difficult one. Department scientists have developed a process for complete disposal of brine wastes and recovery of the salt

for reuse. In this process, a submerged combustion heater evaporates the used brine solution, and impure salt is crystallized and discharged at 60% solids. About 6% of the solids is combustible organic matter; this is subsequently destroyed in a rotary incinerator. The process has been successfully demonstrated on a pilot plant scale, using olive brine. Storage tests have been completed on olives stored in brine made from the salt reclaimed from the previous year's waste stream. A taste panel has been unable to detect any significant difference between the control and the test sample. Preliminary cost estimates indicate a small additional expense in using the reclaimed salt instead of fresh salt. For the average size processing plant, the additional cost for a substantial contribution to pollution control is approximately $2,000 a year, for the first ten years. After the cost of the equipment has been amortized, instead of an added expense, there is a small potential savings of about $400 a year.

Biosynthesis of Iron Transport Compounds to Control Food Spoilage. *Salmonella typhimurium* obtains the element, iron (required for its growth) by excreting iron binding compounds of the phenolate family. These take physiologically bound iron from the surrounding media, and transport it back into the bacterial cell where it becomes available to support growth. Such growth must occur for salmonella organisms to reproduce and constitute a food poisoning hazard. Without these iron transport compounds (ITC), iron would not be available from certain foods, such as raw eggs, because certain egg proteins also bind iron but not sufficiently to keep it from the ITC. These facts have been elucidated by USDA scientists who have also found that the biosynthesis of ITC by salmonella is temperature-sensitive, and operates at 86° F. but not at 104° F. This explains, in part, the role of fever as a natural protection to overcome salmonella infection by elevating body temperature beyond the range of the salmonella capacity to obtain iron for growth. Such biosynthetic reactions may be applicable in defense of other microbial infections. Poultry is a natural reservoir of salmonella infection and remedial measures for control are suggested by these findings. Many strains of salmonella cannot become established, or multiply, at poultry body temperatures of 105° F. and higher. However, young poults have average body temperatures 2 to 3° F. less than adult birds, and are not so resistant. Increasing environmental temperatures at which young poults are housed may prevent synthesis of ITC and growth of salmonella pathogens would cease.

WHEAT

Problems and Objectives

The dominant feature of the wheat economy in the United States is a production capacity that can outpace consumption. Research on wheat seeks to solve the problems hindering the development of markets for the full productive capacity of U.S. agriculture. The emphasis is on expanding overseas dollar markets for U.S. wheats; developing new wheat food products for long-term market development in food-short nations abroad; raising the domestic consumption of wheat foods by increased variety, quality, and convenience; fortifying wheat and wheat products with minerals and amino acids needed in human diets; finding means to upgrade wheat millfeeds to recover fractions of nutritious food quality; and developing new and improved feeds from wheat.

Major objectives of the research are to develop and evaluate alternative ways for: (1) Improving baking properties of bread flours by controlled maturation acceptable in European countries. (2) Developing protein-enriched export foods from wheat flours and millfeed fractions and concentrates. (3) Improving quality of continuous-mix baked goods. (4) Improving quality retention in frozen fermented bread doughs. (5) Improving nutrient quality of wheat foods and using wheat products as carriers for mineral, vitamin, and essential amino acid fortification. (6) Developing processes to enhance the nutritive value of wheat for ruminant, poultry and swine feeds.

Increasing Exports

Steam-pelleted wheat protein concentrate (WPC) (in Flour Blend A) compared with untreated WPC, after storage at 0, 90, and 120° F. showed: lower free fatty acid, little effect on off-odors, and unacceptable bread volume. Antioxidants caused less "rancid" odor but no other effect. Wheat pearling rates and yields improved as grain moisture content increased to 15%. Water sprays (up to 3% by wt.) aided pearling, as did decreasing the hold time between spraying and pearling, and adding $CaCO_3$ abrasive before pearling. A process was developed to treat gluten plant effluent using condensed phosphates to complex and precipitate 99% of protein (88% of N) which is recovered; phosphates are recycled. Conditions for deamidation of gluten have been studied to obtain a dispersible protein at pH 4.3-7.0. "Stickiness" of texturized wheat protein products is reduced by deamidation. Wheat was expanded in hot air (625° F.) and rolled. Raw flavor was lost in 15 sec. at 10% moisture and in 25 sec. at 20%. Starch gelatinization was increased only by increasing initial grain moisture. Gelatinization varies widely in commercial precooked cereals examined. Hot air popping followed by grinding and classification

offers a feasible approach to cheaper pregelatinized flours. Equipment modifications were made for the Fesca protein-starch separation in flour slurries by use of a horizontal decanter centrifuge.

A first clears HRW flour has been processed in a tube-bundle reactor at 106°, 147° and 175° C. over a moisture range of 12 to 35%. Nitrogen solubility changes in treated samples are being studied by using a modified Maes continuous sequential extraction procedure. At mildest conditions a marked reduction in the 2% NaCl, 40% isopropanol, and 3.85% lactic acid soluble fractions and a rise in 0.5% KOH soluble nitrogen were noted; overall solubility remained the same as untreated flour. At more rigorous conditions (147° C.) 0.5% KOH soluble nitrogen drops and thus total recovery drops (to 40% of original). Protein digestibility by pepsin shows decreasing rates with increasing time and temperature of treatment. For example, at 35% moisture, 10 min. and 147° C., pepsin digestion rate is decreased 82% from that for untreated flour. Starch changes are being evaluated by water absorption (WAI) and soluble solids (S.S.). A small but regular rise in WAI occurs at 106° C. and a larger and regular rise at 147° C., with increasing moisture but no significant change due to treatment time. S.S. changed only slightly with moisture and not significantly with time at 106° C. At 147° C. there was an approximate 4-fold increase in S.S. from 12 to 35% moisture; treatment time also showed a significant effect at 147° C. with difference becoming greater as moisture increased. Lysine fortified wheat at 40% moisture was steam cooked 10, 20, and 30 min. at 100°, 116°, and 127° C. and dried under mild conditions. Losses in added lysine averaged 2%.

Research was planned to follow changes in specific components of winter and spring wheat flours during the bread-making process in order to explain the preference for Canadian spring wheats in blends with European wheats. Samples of wheats and flours were collected, but data collected were insufficient to permit firm conclusions relating causes and effects.

In wheat protein concentrate (WPC) at about 16% moisture, heating at 55°-60° C. inactivated 99% of lipoxygenase and about 66% of esterase, and improved baking results slightly. Free fatty acid formation and loss of baking quality was retarded only slightly in storage. WPC of different suppliers differed widely in baking; new specifications for Flour Blend A were written; a baking test was developed to check purchases. Stable free-radical content of wheat milled products rose rapidly severalfold in intense light, subsequently decreased slowly in dark to stable value in air at room temperature. Increased water content generally lowered free-radical content. "Gel" protein solubilized by 0.02 mM mercuric chloride in 0.01 M acetic acid, expressed as % of total protein, was directly related to mixing time and stability as shown by dough mixing curves of 7 widely different flours. Density-gradient ultracentrifugation gave partial resolution of mercuric chloride-solubilized protein components; complexity and distribution of components shown were similar to those by gel filtration electrophoresis.

Field-damaged wheats caused problems in noodle doughs, reduced hot paste viscosities, but showed no visible sprout-damage as judged by Federal grain graders.

Selected Publications

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Food Uses

Frozen unbaked straight doughs with markedly improved stability (exceeding three months at 0° F.) were produced. This was made possible by a combination of factors including: high initial yeast level (5 to 6% instead of the conventional 3%); minimal fermentation time and temperature; use of moderate levels of oxidant ($KBrO_3$); and aging the compressed yeast at refrigerator temperatures prior to use. The increased stability was achieved, however, at the expense of volume, flavor and grain, and a two-stage sponge dough process was then developed which permitted equivalent stability but with markedly improved quality. Preliminary studies were made on the San Francisco sour dough method, originally, with a view to preparing a frozen unbaked convenience product. Although this was not successful, the microorganisms involved in this 100-year old process were isolated for the first time. One, a yeast Saccharomyces exiguus was correlated with the leavening action. The other, a heretofore undescribed strain of Lactobacillus, was correlated with the souring activity.

Four sour dough bacterial isolates were found to be differentiable on the basis of level of maltose required for growth, adaptability to growth on glucose, and percentage of total acidity produced as acetic. Flash-frozen concentrates of two of the bacterial isolates were successfully prepared. They exhibited very good stability at -20° F. and were used in conjunction with cell paste preparation of the sour dough yeast to prepare bread. This bread was virtually indistinguishable from that prepared by the conventional procedure, thus giving the ultimate proof to the role of these microorganisms. A liquid sponge method for making sour dough French bread was

refined and applied successfully in a commercial bakery trial. Partially baked (1/4 to 1/2 baked heat and serve) sour dough bread distributed under refrigerated conditions (35 to 40° F.) was found to be unsatisfactory due to rapid development of shrinkage, staling and off-flavors. However, the partially baked product held up well when frozen and made excellent bread when baked off, even after one to two months'storage.

In contract studies, the sour dough bacterial isolates reported above were subjected to conventional taxonomic tests for biochemical and morphological properties. In accord with prior findings by WMN scientists these tests placed the isolates tentatively in the genus Lactobacillus and also confirmed that they did not coincide with known species. Analysis of DNA showed all four isolates to contain about 37% guanine plus cytosine which virtually coincides with the G+C content of four known species of lactobacilli. This finding lends some credence to the possibility that the sour dough strains are mutant forms of lactobacilli.

Study of the aggregation of alpha-gliadin by light scattering has shown a relationship between formation of the fibrillar aggregates and the conformation of the protein molecule. The unusual aggregation properties of alpha-gliadin have been used to determine the presence or absence of the protein components that make up this fraction in a number of different varieties of wheat. Only a few of the tested varieties yielded alpha-gliadin, but in some this fraction may constitute as much as 10% of the total protein. Disruption of aggregates at temperatures above about 25° C. is evidently related to the unfolding of the protein molecules that occurs at higher temperatures. Calcium stearoyl lactylate, a bread "improver," has been found to complex specifically with the calcium-binding protein isolated from the soluble protein fraction of wheat. Although phospholipid complexes have not proved to be effective alpha-amylase inhibitors, ferrous ion has been shown to inactivate this enzyme in flour extracts at alkaline pH.

Seven wheat flours differing widely in baking quality were studied. Proportions of protein extracted by pyrophosphate buffer, acetic acid, and alkali were not related to baking quality. Sulfhydryl content of glutens was inversely correlated, disulfide content directly correlated with baking quality. Protein disulfide of weak flour glutens interchanged more rapidly with cysteine sulfhydryl (pH 8 in 7 M urea) than disulfide of strong glutens, interpreted as showing a more open, less cross-linked structure in the weak flour glutens. Homogenization to disperse gluten altered its properties; gentle shaking only was recommended. Freeze-drying had no effect. Inactivation of protease by heating of gluten dispersions in acetic acid solutions was not complete in 3 minutes at 100°, nearly so at 5 minutes; 6 minutes were recommended. Concentration of gluten solution by dialysis against polyethylene glycol 6000 was recommended.

Lipoprotein studies included the isolation and characterization of purothionins from wheat; and hordothionins, analogs of the purothionins, were isolated from barley. Other "proteolipids" also were shown to occur in wheat

flour. In the lipopurothionins, bonding between protein and lipid is partly ionic; hydrophobic bonding is minor and hydrogen bonding does not appear to be involved. When flour is made into dough, the lipoproteins are "bound" and are no longer extractable with petroleum ether. The binding of lipids in bread doughs was little affected by work input during mixing over the range of 2 to 6 watt-hours per pound. Reasons for the improving action of fats in conventional doughs, and the critical role of hard fats in mechanically developed doughs, were sought. The mechanism appears to be entirely physical, i.e., chemical oxidation of unsaturated fat or other chemical reaction is not involved. By the addition to bread doughs of solid straight-chain saturated hydrocarbons of varied chain length and therefore of varied melting point, it was shown that no "reservoir" of solid unmelted additive was needed to produce a loaf-volume increase. It is suggested that the "hard" fats provide weak and temporary, but numerous and mobile, linkages between protein chains and perhaps between protein and starch. The formation of many small gas bubbles in dough is thus aided, and crumb grain and texture are improved as loaf volume is increased. It is acknowledged that the lowering of loaf volume observed when baking fats are added to flours that have been de-fatted with non-polar solvents cannot be explained in this way; but de-fatted flours are not of commercial importance.

Mild chlorine treatment of wheat starch increased viscosities of concentrated suspensions at room temperature and of dilute pastes during gelatinization. This suggests surface modifications and gentle loosening of granule structure, allowing more water to be held by the granules. Chlorine dioxide had no effect on suspension viscosity but increased hot paste viscosity. Reconstituted flours containing treated starches exhibited the kind of modified dough and bread properties usually attributed to changes in protein components. These results suggest that surface modification of starch granules affects not only their intrinsic properties but also their interactions with the gluten matrix enmeshing them. Incipient sprouting was shown not only to increase alpha-amylase activity but also to modify starch granule surfaces, as determined by electron microscopy and by analyses of the increased solubles in the sprouted wheat. Metal chelating agents that bind calcium inhibited amylase activity in noodle doughs and in flour-water pastes during gelatinization. Phospholipids that bind calcium and enzyme to form phospholipid-metal-protein complexes were less successful but optimum conditions were not established. Their major effect is at high pH levels (7.0 to 7.5) which suggests their usefulness in Japanese noodles, because they are sensitive to sprout damage and are usually processed at alkaline pH.

A cracker-like aroma isolated from freshly baked bread was shown to be 1,4,5,6-tetrahydro-2-acetopyridine. The compound is also a major reaction product of proline and dihydroxy acetone. The acetopyridine was unstable except as the bisulfite complex or hydrochloride. Ability of the isolate to impart fresh baked odor in stale bread provides presumptive evidence that the compound is part of the fresh baked aroma. The development of appreciable amounts of isobutyl alcohol and acetoin (and their oxidation products isobutyraldehyde and diacetyl) during baking correlated well with

flavor intensity in bread. Thus the levels of isobutyl alcohol and acetoin were roughly 10 times higher in full flavor bread (sponge dough) than in low flavor bread (continuous mix). Storage of the freshly baked high flavor bread for a few days at ambient temperatures led to virtual disappearance of these compounds. The contributions of proline, valine, proline-glycerol reaction product and acetoin to bread flavor were evaluated by their addition separately to the dough at a level of 0.3%. All of these compounds enhanced bread flavor and markedly increased the levels of either isobutyraldehyde or acetoin in the bread. A determination of the sum of the acetoin and diacetyl contents, and of the sum of the isobutyl alcohol and isobutyraldehyde contents, is each recommended as a useful chemical measure which correlates with flavor intensity.

In a contract study of bread dough's unique rheological properties, dough was considered to be a "filled" system, i.e., a continuous hydrated gluten matrix filled with starch granules. Rheological properties were measured to determine in what respects changes in filler material would modify dough. From dynamic mechanical properties of doughs at usual protein levels, aggregates of starch granules exist in undisturbed dough but break down progressively, as sinusoidal displacements of increasing amplitude are applied, until properties are determined solely by the protein matrix. The natural starch granule filler was replaced by particles of glass and some synthetic polymers with little effect on small-deformation behavior. Under large deformation, however, simulated doughs lacked the extensibility of natural doughs. The particle shape, size, size distribution, and surface properties may all be significant factors. Rupture and other large-deformation properties were markedly affected by potassium bromate and N-ethyl maleimide; small deformation properties were little affected. No evidence of a cross-linked covalent structure in doughs could be obtained.

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Feeds

Processing grain to increase its digestibility is an effective way to increase feed efficiency of cattle. This study showed that dry-heat expansion or popping of grains increased in vitro starch digestibility, and gave good results in ruminant feeding tests. Popped products, after grinding, are excellent carriers for molasses or liquid supplements. Results of a sheep feeding test in Texas using milo popped in our laboratory-designed and -built prototype popper (Memorandum of Understanding) were so impressive that a large-scale grain popper has been developed by the cooperating manufacturer for feedlot use.

Wheat bran processed with a turbo mill showed a good increase in *in vitro* protein availability. Pelleting bran gave lower increases. Optimum pelleting conditions have been determined. Pearled whole wheat gave bran fractions with a higher protein content and higher apparent availability than normal bran fractions. Ammoniation of bran yielded products which, by *in vitro* studies, showed good potential as feeds for monogastric animals. Enzymic processing of bran yielded products with high protein availability. At the same time, available energy was increased by partially degrading the cellulosic fiber to digestible monosaccharides. The cellulases used for processing acted by completely degrading the aleurone cell walls. Other cellular structures of bran appeared to be relatively stable to enzyme attack. The in vitro process has been correlated with in vivo rat feeding trials and has been instrumental in predicting the relative nutritive value of wheat millfeed proteins.

Two alpha-amylase inhibitors have now been isolated from wheat flour. There are indications that these inhibitors may be physiologically active.

Selected Publications

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Nutritive Values

Methods are being sought to incorporate ascorbic acid in bread with retention of active forms at nutritionally useful levels and without lowering of bread quality. Because the usual colorimetric method for measuring ascorbic acid gave uncertain values in the presence of interfering substances in bread, a gas chromatographic method was adapted, using the trimethylsilyl derivative of reduced ascorbic acid. Dehydroascorbic acid was not directly detectable by this method. A method was developed for extraction of the ascorbic acid by using sequential chloroform and ethanol solvents. Breads made with added ascorbic acid, uncoated and coated with hard fat or ethyl cellulose, are being evaluated. The complexing of ferrous and ferric ions with various wheat proteins and protein fractions is being studied. Simple electrophoretic methods have not been satisfactory. A hydroxamate iron chelator isolated from Pseudomonas is under evaluation as an in vivo enhancer of iron utilization. Young albino rats were made anemic by feeding a diet low in iron. Then a marginal level of iron supplementation with and without hydroxamate was added to the diets. Analysis of blood samples for hemoglobin indicated that the chelator tended to decrease the absorption of iron, probably by formation of an iron complex within the gut, thereby reducing the amount of iron available for absorption.

Controlling Pollution

Equipment and techniques have been developed to process cellulosic wastes on the laboratory scale and estimate their potential usefulness as ruminant feeds. Processing involves treatment of straw and other high-fiber products with steam, sodium hydroxide, calcium hydroxide or ammonia at different temperatures for various periods of time. Commercially available enzymes are used to digest the treated products and evaluate the effects of treatment. The enzyme assay correlates very well with in vivo results. Digestibility of many materials can be increased from 50 to 150% by processing. Equipment is being assembled to prepare large enough quantities of high-pressure processed and pelletized straws for animal feeding tests. Two samples of rice straw processed at atmospheric pressure with

4% sodium hydroxide at 100° C. (one for 15 minutes and one for 60 minutes), have been fed to sheep in a digestibility trial. Dry matter digestibility of the treated straws were 53 and 59%, respectively, compared to a value of 38% for the control. A sample of rice straw treated with ammonia for 30 days at ambient temperature showed a digestibility of about 50% with sheep. No detectable amounts of potentially toxic 4-methyl imidazole were found in the ammonia-treated rice straw.

Results of contract work at the University of Nebraska indicate that high pressure treatment of corn cobs with steam, or with steam and metabisulfite, increases their apparent in vitro digestibility. However, animal feeding tests show that animal performance is less than anticipated from the in vitro studies, and that an inhibitor is apparently generated during the high pressure processing step. Further work will be required to determine ways to overcome or prevent inhibitor formation.

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RICE

Problems and Objectives

The per capita consumption of rice in the U.S. has increased about 25% over the past ten years. Most of the increase has occurred through the use of processed products featuring convenience of use, especially quick-cooking rice. Most of this product is made by processes which are inefficient due to rather large losses of solubilized solids and to kernel breakage. Final product cost is therefore higher than necessary. Also all precooked rice is made from long-grain rice, which is higher in cost than medium- or short-grain rices. The need is for new and improved food products with better nutritive quality and produced at minimum increase in cost. Such products must be easy to prepare; have good texture, flavor, and appearance; and be economical to manufacture. Also needed are drastically improved milling methods. Disposal of rice hulls is a major problem for the rice milling industry; methods for converting waste rice hulls to consumer products are needed.

Major objectives of the research are to develop and evaluate alternative ways for: (1) Developing new processing methods for lower cost consumer products from short- and medium-grain rices. (2) Developing new products from waste rice hulls. (3) Converting rice straw to feed. (4) Controlling contamination of toxin-producing microbes in stored rice.

Controlling Pollution

Preliminary technical and economic feasibility analyses of 15 concepts for the utilization of rice hulls were proposed, along with detailed treatment of 4 promising concepts. The conclusions for the latter concepts were: (a) cement manufacture with rice hulls is technically and economically feasible for the Sacramento Valley area; (b) manufacture of architectural boards is possibly promising by several methods, and would be economic for most rice growing areas; (c) manufacture of silicate structural materials appears feasible by several methods, most promising by autoclave bonding; and (d) sodium silicate could be made by several approaches and would be most economic in the Sacramento area. Additional technical work is recommended on several novel approaches to the suggested manufacturing processes.

Production of silicon tetrachloride from rice hulls will involve pyrolysis, followed by chlorination at a high temperature in the absence of water vapor and oxygen. About 56 experimental runs conducted so far have shown that a minimum time-temperature exposure for pyrolysis is required, above which no improvement in chlorination is found. The exact minimum conditions have not been found but they are known to be less than 850° C. for 30 minutes. In the range 715°-1260° C. chlorination appears to occur in two steps, one very fast (on the order of minutes) and the second so slow that it is difficult to detect. The fraction of silica reacted during the fast period increases from about 40% at 700° C. to about 75% at 1200° C.

Publication

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Food Uses

Three high-protein flours, abrasively milled off as consecutive layers from each of 6 different milled rices of one crop and 6 (2 parboiled) of other crops and locations, were compared with original and residual kernels. The following were determined: milling data, moisture, protein, amino acids, ash, lipid, starch, amylose, phytic acid, calcium, phosphorus, sodium, potassium, iron, thiamine, riboflavin, niacin, pyridoxine, viscosity and cooking properties, stability, odor, and flavor. PER value, by rat feeding, for 20 flours and fractions was 2.03 $\pm$ 0.20 (casein = 2.5). Amino acid balance in flours differed little from that in residual kernels. One flour removal (of about 3% of kernel) seems best; a second removal flour was almost as good. These data indicate that high-protein flour, rich in many nutrients, is easily produced in one or two operations by standard equipment without loss in amino-acid balance, leaving residual kernels of good quality.

Glutinous rice having only amylopectin type starch contained soluble starch synthetase; the usual form is granules-bound. The soluble enzyme bound strongly with amylose, much less so with amylopectin; enzyme properties were not affected. The binding property enabled 300-fold purification of starch synthetase and should be useful in starch column chromatography. The soluble synthetase specifically required adenosine diphosphate glucose (ADPG), but the granules-bound form used UDPG (uridine compound) as well; resulting starches were, respectively, largely amylopectin and equal proportions of amylose and amylopectin. Potassium ion stimulated slightly the granules-bound synthetase. Rice starch degradation during germination was chiefly amylolytic (alpha-amylase and maltase) with little phosphorylase activity. Glucose formed was converted in the scutellum to sucrose which was utilized. During germination four major and several minor isozymes of alpha-amylase were detected. Seven reports are published; two are in press. The basic advances in knowledge of starch biochemistry, particularly about soluble starch synthetase, increase understanding of variations among amylopectins, which appear to affect cooking and processing properties of different rices.

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Microbial Contaminants

Chromatograms of chloroform extracts of cultures of Aspergillus candidus, A. Niveus, Penicillium citrinum, P. oxalicum, P. piceum and P. rubrum were run. P. citrinum had spots corresponding to aflatoxin B_1 and luteoskyrin and P. rubrum spots corresponding to rubratoxins A and B.

Culture filtrates were concentrated 20 times for toxicity studies. Two one-ml. doses of concentrated P. citrinum filtrate were lethal to 50% of the white leghorn chicks. One-half ml. of concentrated P. oxalicum filtrate was lethal to 50% of the birds. Even 0.5 ml. of concentrated A. candidus filtrate was lethal to 100% of the birds.

Swiss albino mice died after four one ml. feedings of concentrated A. candidus filtrate. There was 50% mortality after 15 days of feeding one ml. doses of concentrated filtrate of A. niveus or P. citrinium.

Mitochondria from P. rubrum poisoned mice livers were tested for damage to several of their enzymatic activities. The release of inorganic phosphate in the presence of DNP and the P/O ratio were both reduced while the oxidation of 2-oxoglutarate in the presence of DNP was accelerated in the poisoned mitochrondria. Microsomal glucose-6-phosphatase was also inhibited.

Increasing Exports

Brown rice was coated with glucose plus talc or Ca citrate with or without BHT (antioxidant). Accelerated storage tests (closed bottles) are underway. Initial results (5 months) show little effect on free fatty acid but suppression of oxidative rancid odor by BHT. A suitable method was developed for assay of lipase activity in rice bran. Salt and solvent precipitation of extracted lipase has given 52-fold purification; gel filtration is now being used to increase this and get molecular size data. Extraction of full-fat bran with sodium hydroxide at pH 11 (optimum) gave 50% of total protein as a 60% concentrate; alcohol wash of this material gave a light-colored product with 37% of total protein as 85% concentrate. Bread made from 6% protein rice flour (no wheat) by modern starch-bread methods had good loaf volume and crust and fair crumb in early trials. Bread from 12% protein rice is also good; that from outer-layer, full-fat rice flour is not as good. Component variations cause much quality change. Prospects seem bright for a good hypoallergenic rice bread. Amylograms of three consecutively milled outer-layer high-protein flours from ten raw and two parboiled rices, and for original and residual kernels, are completed. Outer flours gave lowest viscosities; residual kernels highest. Indicator amylogram points correlate directly with starch content and inversely with protein content of flours.

FORAGES

Problems and Objectives

The demand for livestock in the United States will increase about 33% by 1975. Since forage crops constitute the major feedstuff for ruminant animals, the demand for forages will increase accordingly. In addition, there is an increasing demand for processed forages in European and Asiatic markets as well as in domestic markets. Fresh forage crops are the richest natural source of many nutrients for farm animals. However, up to 30-40% of the forages are lost during haymaking and ensiling. Dehydration is now the only practical means of producing products of high nutritional value in a form usable in manufactured feeds and supplements, but use of dehydrated products is restricted because of their high-fiber and growth-inhibitor content. New and improved products are needed for foreign and domestic markets.

Major objectives of the research are to develop and evaluate alternative ways for: (1) Improving feeds from alfalfa and other forage crops. (2) Improving ruminant feeds from highly lignified fibrous agricultural materials. (3) Developing products containing standardized amounts of unidentified growth and reproduction factors (U.G.F.). (4) Developing new low-fiber products from forage crops for export markets. (5) Recovering feed and other values from high roughage field and processing residues.

Feeds

A good market has developed for PRO-XAN, the product of wet fractionation of alfalfa. A second producing unit is being planned by our commercial collaborators. Other dehydrators in this country and abroad have contacted us in regard to installing the process. Improvements have been made in the unit processes. These include the installation of a second larger set of rolls and an improved method for separation of the protein coagulum. To eliminate recycling during drying, a pilot-scale filter press to increase solids content from 20 to 40%, is now under development.

One cattle-feeding experiment was completed; it used two levels of alfalfa solubles in liquid supplements containing high levels of urea. Liquid distiller's solubles were used in supplements for the positive control; all three supplements were compared with the standard Purdue Liquid 64. The lower level of alfalfa solubles produced the highest rate of gain ($P<.05$) at the lowest cost. However, contrary to previous results, the distiller's solubles produced no improvement over Purdue Liquid 64. Also, the higher level of alfalfa solubles produced no improvement. Further study will be necessary to clarify the apparently discordant results. Alfalfa solubles increased nitrogen retention by steers by about 20%.

Large losses of xanthophylls were found to occur during alfalfa dehydration, unless outlet temperature and meal moisture were carefully controlled. The

epoxy xanthophylls, violaxanthin and neoxanthin, were found to have no pigmenting activity for broilers. A method was developed to exclude these from xanthophyll analysis. Alfalfa harvested during the summer months contained higher levels of pigmenting xanthophyll than that harvested in the fall.

Separation of alfalfa saponins on alumina columns resulted in the isolation of the individual saponins. The nature of the sapogenin as well as the sapogenin/sugar ratio contributed to the haemolytic activity of the saponins. Alfalfa sapogenins were found to be more toxic toward larvae than their respective saponins. Medicagenic acid and an unidentified sapogenin were found to be the main agents responsible for inhibiting larvae growth. This effect was reversed when cholesterol was added to the diet. The inhibitory effect of alfalfa saponins on the germination of cottonseeds was attributed to interference with the seedcoat and the membrane rather than impermeability to water.

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WOOL AND MOHAIR

Problems and Objectives

Traditional markets for wool and mohair have been lost to synthetic fibers because consumers prefer garments that hold their pleats and creases, resist shrinkage and wrinkling during washing, and dry quickly. Natural wool and mohair outclass the synthetics in tailorability, comfort in wear, appearance, and hand, but lack certain features now being exploited by the promoters of synthetics. Furthermore, some current processing methods damage, distort, or weaken wool and mohair fibers and injure performance and appearance of the fabric. We need processes that will modify natural fibers to give a range of comfortable and attractive fabrics that resist deterioration in processing and wear. New markets in industrial and other uses would develop for new types of fabrics, woven and non-woven, made from natural wools and from blends of wool with modified wools or other fibers.

Major objectives of the research are to develop and evaluate alternative ways for: (1) Developing improved fabrics from wool and mohair blends. (2) Improving efficiencies in the processing of worsted wool and mohair yarns. (3) Developing treatments for wool and mohair products to decrease upkeep costs. (4) Controlling pollution and conversion of the waste products of wool processing.

Yarns and Textiles

Low temperature plasma treatment of wool was further simplified. A portable treating unit was built and coupled to a knitting machine. Not only is wool made shrinkproof by this treatment, but yarn strength and abrasion resistance are increased. Studies indicate that the set-up is suitable for larger scale, multiple yarn treatment. Excellent durable press in 100% wool fabric has been obtained by applying a polymer for shrinkproofing, followed by pressing in the presence of crosslinking and reducing agents. New high molecular weight copolymers of a fluorinated methallyl ether and maleic anhydride show interesting soil-release properties on wool-blend garments.

Corona treatment reduces felting shrinkage in wool and mohair. Optimum treatment occurs at or above a temperature of 85° C. with frequency and voltage approximately 2000 Hz and 15 kV, respectively. Reaction rate is increased by the injection of dilute chlorine gas into the corona cell. Polar sites, some of which have been identified as sulfonic acid groups, are created on the fiber surface. Wettability in water is increased and electrostatic behavior is altered. The position of wool or mohair at the positive end of the triboelectric series may be shifted toward the negative end to make these fibers electrostatically neutral to various insulators such as leather or rubber. This effect has practical application for wool or mohair carpets. Normal positive, and corona-treated negative, fibers

may be blended to increase cohesion and improve spinning. Soil repellency is increased by corona treatment because soils are generally negatively charged and are repelled by the negative fiber surface. Treatment with a cationic surfactant reverses effects of corona treatment on wettability, friction, and shrinkage. Wool and cotton fiber friction, and roving cohesiveness, are very high immediately after corona treatment but diminish in a few hours to a constant level somewhat above the original value. Improved mohair carding, and wool and cotton spinnability, result, and the tensile strength of wool, mohair, and cotton yarns is increased; hairiness is decreased. Cotton fabric abrasion resistance is increased 50%.

Materials needed to study yarns and fabrics consisting of blends of untreated and corona-treated wool, mohair and cotton have been purchased and are being prepared for testing.

Development research and in-plant trials were carried out on interfacial (IFP) polyurea systems, involving stepwise treatment with diamines and diisocyanates of batch knitwear, continuous fabric, blanket, and top. A prototype, automated processing unit was designed and built for batch shrink-resist treatment of wool knits based upon IFP reaction of ethylene diamine (EDA) in aqueous solution and methylene bis(4-phenyl isocyanate) (MDI) in petroleum solvent solution. Commercial knitwear manufacturing plant and production trials were conducted. Process was most successful for knit goods normally wet finished, wash or fulled. Main limitations were tendency of finish to yellow in sunlight, distortion of stitch clarity, and whitening in tightly knitted structure. Plant tests of continuous fabric woolen treatment with EDA/MDI polyurea system established technological operability, dyeability of treated fabric, excellent aesthetics, and effective shrinkproofing. Control of relaxation shrinkage is less effective with EDA/MDI than IFP polyamide. Plant demonstration trials on wool blankets show superiority of IFP polyurea over IFP polyamide or oxidative shrinkproofing. Limited trials with hexamethylene diamine (HMDA)/MDI for top treatment indicated poor dyeability of treated top.

Previous work on the dimensional properties of plain-knit structures in machine washing and tumble drying has been extended to more complex knitted structures. In contrast to plain knits, rib structures (1 x 1 rib and half-cardigan) knitted from WURLAN shrink-resist treated wool top exhibit anisotropic behavior (decrease in length and increase in width) in repeated laundering and drying. Among double knit structures, Swiss double piqué fabrics, consisting of a plain unit and float units, made from treated wool, are dimensionally stable in repeated laundering, provided fabrics are fully relaxed by wet tumble drying. Interlock structures, an example of double knit fabrics knitted from rib loops only, exhibit anisotropic dimensional behavior in laundering similar to 1 x 1 rib and cardigan structures. For all of these complex knit structures, empirically derived dimensional parameters, based upon the Structural Knit Cell concept, have been determined. These structural parameters permit rational design of complex wool knit structures for machine launderability.

Experimental wool-polyester blended fabrics have been woven, dyed and finished. They will serve as standard material in wool blend durable press studies that will evaluate newly developed wool stabilization and setting procedures. Previous work on durable press blends with adult mohair has been extended to include kid mohair. All three mohair-rayon-polyester blends studied, 50-30-10, 40-40-20, and 1/3-1/3-1/3, have excellent aesthetic and wear properties, combined with outstanding durable press performance in washing and tumble drying. Results were not very different for kid mohair and young adult mohair in the final blended fabrics except that fabrics made with kid mohair had a slightly better fabric hand. Kid mohair is a premium priced fiber, compared to the moderate price of adult mohair. Either grade of mohair would contribute luster, crispness and unique aesthetic properties in blends with polyester and rayon. Unlike wool, mohair blends in a tight slack fabric construction do not require shrink-resist treatment and can be processed and treated in the same manner as other durable press blend fabrics.

Woolen fabrics were soaked in the presence of a detergent and an enzyme preparation used in home laundry formulations. The enzyme weakens the fabrics. The loss in strength is accompanied by a loss in weight.

Recent work shows that wool is made more resistant to chemical attack by treatment with divinylsulfone in dimethylsulfoxide, presumably by crosslinking. Quantitative modification of sulfhydryl groups by 2-vinylpyridine in reduced wool permits quantitative determination of cystine by two independent techniques: ion-exchange chromatography and ultraviolet spectroscopy. This new analytical procedure for cystine in wool is suitable for routine analyses.

Surface roughness and mechanical properties of individual fibers were studied. Experimental and practical degradative treatments to control shrinking also clearly increased roughness. Roughness was found inversely related to felting. Taken together, roughness and mechanical properties indicate whether a fiber has been effectively treated and the extent to which treatment has been confined to the surface. The finer fibers are the more easily damaged. Scanning electron microscopy (SEM) clearly shows surface changes due to the more severe treatments. Treatments differ in the kind of change produced. For instance, surface cracks resulted from treatment with chlorine gas or alcoholic alkali, while permanganate gave gradual scale erosion. Wool and mohair respond differently: mohair was more susceptible to surface cracking. SEM appears not very useful for showing changes due to mild degradative treatments of practical interest, except to get evidence of fiber variation and nonuniform treatment.

A new model for the mechanical behavior of wool fibers called the G-H model, was developed, postulating axially oriented non-helical or G protein chains in parallel and in series with two kinds of alpha-helical protein. G component is as important as H component in extensional behavior. The model accommodates all known experimental evidence. It permits predictive explanation of crosslinking effects, wool contraction, and

wrinkle behavior. Axial orientation of microfibrils was explained by a simple statistical mechanical model of rods constrained in a cylinder. Hydration effects on glass transition temperatures can explain fiber characteristics important in wrinkling. Felting shrinkage was found to depend in part on interfiber hydrophobic bonding, hydrophilic treatments reduced the felting aggregation and shrinkage. New ASTM tests were written and evaluated for moisture determination, and evaluations were made of fabric and fibers after various chemical modifications.

Previous work showed that wool fibers illuminated by polychromatic light gave rise to a complex radical population and suggested that simpler results might be obtained if monochromatic light and controlled dose rate were used. Accordingly, light filtered to give wavelength in the blue region from 4000A to 5000A was selected as most likely to produce free radicals based on the absorption spectra of keratin. Under these conditions the radical population appeared to consist of an initial stable radical insensitive to radiation and three other radicals, two of which followed decay kinetics different from the third. A new mechanism to account for the experimental curves of radical concentration vs. radiation dose is suggested in which the decayed radicals form sites immune to further radiation. A study of decay kinetics showed that experimental results were best fitted by second order processes. Of the three radical species, two have similar decay kinetics while the third has considerably different kinetic behavior. It is also concluded that all of the radicals produced by blue light may result from breakage of the NH or CH bond and are not believed to be due to main chain scission or rupture of the peptide bond.

The titrations of natural wool with HCl, H_2SO_4 and with H_3PO_4 do not allow a clear choice between the Donnan model and the Gilbert-Rideal model of wool. The titration results suggest that ionizable groups inside the wool structure are not very close together. The effects of oxidation of wool with iodic acid, periodic acid and perchloric acid on wool solubility, supercontraction and set was studied and interpreted in terms of stability of alpha-helices in the wool structure. Titration shows that oxidized wool is more acidic than natural wool, partly due to the formation of SO_3H groups. The results should be useful especially for a rational approach to the dyeing of wool.

Work continues on the investigation of wool fibers and simpler systems which simulate various aspects of wool structure. The inelastic neutron scattering curve for 1,3,5-triamino-2,4,6 trinitrobenzene have been determined. Several of the low frequency absorption bands, which are due to modes involving extensive motion of the protons, have been interpreted, in terms of molecular vibrations and rotations of the NH_2 groups and modes which mix with them.

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CITRUS AND SUBTROPICAL FRUITS

Problems and Objectives

The economic stability of the citrus and subtropical fruit industries in the Western Region is dependent upon effective utilization of fruit that cannot be accommodated on the fresh fruit market. Ineffective utilization of products is continuously increasing processing costs and resulting in decreased returns to the grower. Also, deterioration of flavor and color in processed citrus and subtropical fruit products imposes severe limitations upon the economic stability of the industry. New and improved fruit products are needed. The reduction of water pollution is another critical problem for the fruit processing industry. Needed are methods for processing brines so as to reduce the effluent salt contents of processing plants.

Major objectives of the research are to develop and evaluate alternative ways for: (1) Improving stability and flavor of non-frozen fruit juice concentrates and purees. (2) Developing citrus products with improved flavor, color, and stability. (3) Processing mechanically harvested dates. (4) Developing sweeteners from citrus flavonoids. (5) Controlling pollution and converting waste products.

Food Uses

Changes in cellulase activity during ripening of Deglet Noor dates were studied. The activity was absent at the green stage, but mature dates possessed a relatively high amount of activity. The activity began to develop during the period in which the fruit matured from the green to the early red stage. A sharp increase was observed during the period that the fruit ripened from the red to the late red stage and the activity remained fairly constant during further ripening. The enzyme had an optimal pH at 5 and was relatively heat stable. A treatment at 40° C. for 5 minutes had no effect on activity, a 60° C. treatment caused 27% loss while 80° C. caused 84% loss when compared to the control held at 0° C. The results obtained in this study coupled with results reported previously suggest that date cellulase plays an important role in the ripening and softening processes. An attempt was made to control activities of hydrolytic enzymes such as cellulase, polygalacturonase and invertase, which are present in dates, by using plant hormones during post-harvest treatment. Auxin, abscisic acid, kinetin, gibberellin and ethrel were used, but no effect of these hormones was observed on changes in the level of enzymic activity.

Improved techniques were developed for separating the hydrocarbons and oxygenated compounds in lemon oil and for subsequent estimation by gas chromatography of more than 100 constituents contained in these fractions. Important differences were observed in the composition of Desert and

Coastal type lemon oils. Rapid bleaching, loss of flavor, and development of off-flavors occurred during storage of whole, cold-pressed lemon oil in sealed, flint, but not pyrex glass, bottles exposed to fluorescent light and ambient daylight in the presence of trace amounts of water, citric acid, and ionic copper and iron. Development of off-flavors was concurrent with formation of p-cymene and losses in several terpene hydrocarbons. Loss of flavor appeared to be related to losses in neral and geranial and their apparent conversion to two compounds identified tentatively by micro IR, NMR, and mass spectrometry as δ-8-p-methene-1,3-diol and its 3-formate ester. Terpene hydrocarbons, constituting more than 90% of lemon oil, appear to be primarily responsible for off-flavor development and to contribute indirectly to changes in the oxygenated compounds which are the principal flavoring constituents. A process was developed for the preparation of high-quality terpeneless lemon oil. The use of terpeneless oils should enhance the stability of lemon-flavored food and beverage products.

In addition to two reported previously, four chemicals were discovered that cause enhancement of color in citrus and other carotenogenic tissues. These additional compounds were chemically synthesized; they offer the potential of enhancing the natural color of citrus fruits and other agricultural crops. Data on the individual amino acids of citrus juices were gathered to further characterize the juices. Significant changes with maturity, variety, and growing area were noted in several of the major amino acids. Treatment of citrus fruits with various chemical agents several days before juicing is an effective approach to reducing the limonin-caused bitterness of the juice. The approach appears particularly useful in reducing the bitterness of navel orange juice. Studies are underway to determine the optimum conditions of treatment. Results of a survey on microorganisms capable of metabolizing limonin showed that bacteria obtained from soil could convert limonin to nonbitter compounds. The existence of enzymes capable of debittering limonin is thus established. Particle size and density distribution estimates were obtained for fresh, unpasteurized lemon juice. Fractionation of the particles was shown using a zonal rotor procedure.

Fruit beverage bases for 5 + 1 dilution were preserved by pasteurization and addition of antimycotic additives; separation of insoluble solids was minimized by addition of gums or alginates. Organic acids in papaya were citric (35%), malic (30%), ascorbic (20%), α-keto glutaric (2.5%); and tartaric, galacturonic, pectic, and volatile acids make up the balance. Citric acid is the predominant acid in both yellow and purple passion fruit; relative amounts of lactic, malonic, malic, succinic, tartaric and other acids differ with the variety. Unit operations in mango puree processing which represent new innovations include steaming whole fruit, disintegration with a power cutter-stirrer, and centrifugal separation of seeds from pulp and pieces of skin. Papaya puree quality is enhanced by steaming whole fruit before slicing and scraping, then lowering the pH to 3.5 by addition of citric acid immediately after disruption of the tissues. Research is conducted in cooperation with Hawaii Agricultural Experiment Station, Dole Company, Hawaiian Juice Industries, Inc., Hawaiian Banana Co., Suisan Co., and Kaaawa Farms Co.

A number of new dihydrochalcones have been prepared in continuation of studies on structure-activity relations in this series. A few of these compounds have some promise as sweetening agents; two others may have some potential as antioxidants. A reagent has been discovered that appears to be highly specific and sensitive for detecting certain types of dihydrochalcones. This reagent, which can be used in solution and on paper or thin-layer chromatograms, should facilitate detection and analysis of dihydrochalcones in foods and beverages.

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DECIDUOUS FRUITS AND TREE NUTS

Problems and Objectives

Fruits and nuts are valued for their unique flavor, color, and mineral and vitamin content. At harvest time, markets are glutted and growers often do not get an adequate return. Processing makes these commodities available all year and opens new markets for producers, but the unique qualities of these crops are not easily preserved by processing. New and improved products for domestic and foreign markets are needed. The control of microbial contaminants in products and the reduction of water pollution by reducing processing wastes are also critical problems for the processing industry.

Major objectives of the research are to develop and evaluate alternative ways for: (1) Developing dried fruit and tree nut products acceptable to foreign markets. (2) Controlling microbial contaminants of fruit and nut products. (3) Evaluating processing characteristics of Pacific Northwest berries and fruits. (4) Improving stability and flavor of non-frozen fruit juice concentrates and purees. (5) Evaluating changes in fruit pigments during processing. (6) Improving piece-form and powdered dehydrated fruit products. (7) Improving processes for wines. (8) Reducing processing wastes from peeling of fruits to minimize pollution. (9) Determining changes in pesticide residues during processing.

Processing New Varieties and Mechanically Harvested Fruits

Freezing characteristics were determined for six strawberry hybrids and Northwest and Hood strawberry varieties from four widely separated growing areas in the Pacific Northwest. As in 1969, only two of the hybrids were satisfactory for freezing. One of them, WSU 1239, has been named "Shuksan" and released for commercial propagation and growing. WSU 1232 is scheduled for possible release in late 1971. The four unsatisfactory for freezing have been eliminated from further testing. In 1970, Shuksan was superior to Northwest in flavor, appearance and texture, but had poorer color. Preserves made from the berry compare well with the product made from established preserving varieties. Shuksan had higher acid, soluble solids, anthocyanin pigment, and ascorbic acid content than Northwest. The mean ascorbic acid content for the variety was 74 mg. percent, making it a very good source of Vitamin C. Of red raspberry varieties and a hybrid tested, Matsqui (a Canadian introduction) had the best quality as a frozen berry. Eight varieties and 31 hybrid blueberry selections were evaluated for processing potential. More than a third of the selections will be dropped because of poor processing and field performance. However, several hybrids from the USDA Crops Research Division in Beltsville, Md. are well adapted to production in the Pacific Northwest and have potential as commercial varieties for this region.

Experimental lots of Concord grapes, grown under controlled horticultural conditions, were harvested, and the grapes processed into juice; samples were sent to WMN for evaluation and analysis. Variables studied are three different spacings of the double curtain trellis at three pruning levels. Four additional samples came from potassium-deficient vines to compare their tartrate content to juice from normal vines. Wines made from red varieties grown in the Prosser, Washington area were high in pH even when titratable acidity was in an acceptable range. Potassium content of the wines varied from 360 to 1165 mg/l for white and from 1010 to 2470 mg/l for red wine. Preliminary investigations indicate pH and titratable acidity are related directly to length of exposure of the juice to the skins. Four methods of preparing samples of fresh grape berries for testing soluble solids, titratable acidity and pH are under investigation. From the 1970 harvest 55 lots of experimental wine for evaluation were made from 48 grape varieties, 29 white and 19 red; of these, 17 were hybrid and the rest vinifera.

Various procedures have been used in conjunction with drying and mechanical harvesting of grapes. An oleic acid spray on the grapes, while they are still on the vine, seems to have the greatest possibility. The skins of grapes thus treated become very permeable to water, so the grapes will dry readily on the vine. The raisins thus dried have a brown color and show more variability in color than raisins produced by conventional method. A number of treatments were also used on hand-harvested and mechanically harvested grapes. The grapes were sun-dried and dehydrated after treating. Quality evaluations of the product raisins are in progress.

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Food Uses

It has been shown that blending of Thompson seedless grape juice with low sugar juices (e.g., pomegranate) results in pleasing, thirst-quenching beverages. Bland grape sugar for food industry use has been prepared (with recovery of tartaric acid) at a price competitive with beet sugar. A method of separation of anthocyanins from other phenolics by means of anion exchange resin chromatography has been developed. Information has been obtained on many of the flavor constituents of various juices. New filtration methods for grape juice have been developed. A new method of osmotic concentration of grape juice was developed by which water is removed from the juice across a semipermeable membrane into a hypertonic solution. An extension of this method is a manner of osmotic dehydration of particulate foods using an edible cast membrane. Calcium pectate and calcium alginate were successfully used as membranes.

New methodology was developed and used for improved analysis and identification of volatile components of fruit and fruit essence. Pilot plant

equipment was built for scale-up of laboratory procedures for liquid CO_2 extraction of fruits and fruit essence. Carbon dioxide is an efficient extraction solvent having the advantages of low boiling point and lack of toxicity and flammability. Aroma concentrates from CO_2 extraction contain little water content and so should be especially useful in low-moisture fruit products.

Benzoic acid was found to be effective in controlling mold and yeast growth on high-moisture prunes. It may substitute for sorbic acid, but its taste threshold is low. In connection with this study, new methods were developed for detection of parasorbic acid impurity in sorbic acid. New antimicrobial compounds developed under RA 604-08-213 were tested. Cinnamyl phenols are active antimicrobial agents in the pH range 3-6. A new series of raisin samples were distributed to collaborating analysts for moisture determination in conjunction with developing a recognized official method for determining moisture. Plant catechol O-methyltransferase was found to consist of two enzymes, one methylating at the 3-position on the aromatic ring (involved in synthesis of lignin and anthocyanins), the other at the 4-position (synthesis of some alkaloids). Since O-methyltransferase has an optimum pH of 8.5, alkaline dips were used to prolong storage life of refrigerated apple slices. Some sulfite or ascorbic acid, together with calcium in the alkaline dip, produced the longest refrigerated storage life.

Application of the Uni-flow filter to three steps in wine making (carbon treatments, lees filtration, and still slops treatments) has been studied. This filter makes possible a new method of carbon treatment--powdered carbon cascading--a method offering the advantages of both the large surface of powdered carbon and the "front" formation of a column. Lees and still slops may be filtered to less than 5 mg/l suspended solids. A Uni-flow filter-ion exchange process pilot unit for still slops treatment is being designed. Botrytis cinerea bonification is accepted by at least two wineries and will be used commercially when FDA approval is secured. A continuous champagne production test unit has been designed and built and is ready for testing. Studies on a new system for insolubilizing enzymes using tannic acid-glutaraldehyde or collodion membrane-glutaraldehyde were reported at the annual meeting of the Wine Institute (June 17, 1971); potential applications in wine and beverage processing were discussed. Changes in the aroma makeup of a Zinfandel wine are being monitored in a continuing study of wine aging, because an important factor in the improvement of a red wine with age is the development of a fine bouquet, or aroma. A knowledge of such changes will be of value in attempts to hasten the aging process.

The study of browning of wines revealed more pronounced browning in wines from mold invaded grapes than from healthy fruit. Higher polyphenolase activity was found in must and wine made from moldy grapes than healthy ones. More phenols found in wines made from moldy material than mold-free grapes. SO_2 addition to must prior to fermentation prevents browning and preserves phenolics intact. Addition of ascorbic acid without SO_2 has a temporary color preserving effect; exposure to air nullifies it. Bentonite

treatment retards browning for a few months. Color inducing effects of 27 strains of yeast were studied and additional yeast strains are under investigation in hope that a proper yeast may reduce browning. It was further found that rapid liquid-solid separation effectively diminishes browning. It appears that a combination of the methods outlined, while not shedding any new light on the problem so far, may alleviate browning of wines.

Chemical mechanisms involved in fruit pigment deterioration were studied. Oxidation of anthocyanidins to colorless phenolic compounds depends on pH and presence of alcohol. Reaction products included physiologically active 2-phenylbenzofurans and keto diols which readily reduce to colorless leucoanthocyanidins. Anthocyanin reduction to complex dimers or to colorless flavenes was demonstrated. At pH 3-6 anthocyanidins lose 50-70% of their color by forming a complex reversible equilibrium with their corresponding anhydro base, carbonyl base and chalcone. Equilibrium is affected by light which involves photo isomerization of the trans-chalcone to the cis-chalcone which then cyclizes to the flavilium salt. Color variation produced by the same anthocyanin in different fruits and flowers is due to the formation of complexes with iron and aluminum and stabilizing natural co-pigments. Co-pigments were identified as phenolic flavones and catechins which produce blue stable pigments. Formation of anthocyanidins from colorless precursors was shown to be possible by simple isomerization of some flavanones and by quinone oxidation of flavenes. Condensation reactions of leucoanthocyanidins and cinnamyl alcohols with polyphenols to form model tannins and neoflavanoids were determined. It is proposed that the complex red tannin pigments of wines are formed similarly by anthocyanidin and leucoanthocyanidin-polyphenol condensation reactions.

Freezing behavior of fruit juices and sugar solutions was studied by means of differential scanning calorimetry. Initially, concentration polarization inhibited ice formation (as distinguished from nucleation) whenever interstitial solute content reached 70%. The principal mechanism of ice nucleation appeared to be the newly-identified process of secondary nucleation, that is, nucleation induced by pre-existing ice crystals. Nucleation was subject to inhibition by pectin. A seeding technique was devised to increase the amount of ice formed. Slush-frozen orange, grape, and apple juices were concentrated by vacuum evaporation. After evaporation of over half of the water originally present, 70-90% of monitored non-aqueous volatiles were retained. Distribution of residual volatile compounds (e.g., ethyl acetate, ethanol, 1-limonene) in the concentrated matrix was determined. Results confirmed a mass transport model based on ternary diffusion theory. Slush-concentration offers possibilities for 3-6 fold juice concentrates with superior flavor retention, and may lead to an improved method for complete dehydration.

Four out of six brands of pectolytic (juice-clarifying) enzymes impaired apple juice aroma, by gas chromatography and sensory tests. Two brands had little effect, but more work is necessary for verification. Normally harvested apples were stored 11 weeks at 10° C.; and emanations from whole apples, enzyme-deactivated homogenates, and juices were analyzed each week. These three samplings gave widely different concentration ratios of

individual volatiles. At four weeks (optimum juice quality) in comparison of emanations to juice, aldehydes were nil to high, alcohols low to high, C_{10-12} esters very high to very low, respectively. Levels were intermediate in homogenates. Butyl and hexyl acetates were substantial in all three. Concentration of these esters in emanations may be an indication of optimal harvest date. Relative concentration of individual volatiles in the juice varied with storage time before pressing. At the beginning of fruit storage, aldehydes predominate; at four weeks, esters; and after six weeks, alcohols are highest. Alcohols appear at least partly responsible for over-ripe aroma after the fifth week. Enzyme extracts from apple skins converted valine, leucine, and isoleucine to isobutanol, 3-methylbutano-1-ol, 2-methylbutan-1-ol, respectively. ^{14}C-labeled isoleucine injected in whole apples was partly converted to hexyl 2-methylbutyrate, which is considered to be one of the most important esters.

New studies on inhibitor-bound column chromatography are being conducted at the forefront of enzyme methodology. This method may prove particularly useful in the historically difficult field of phenolase purification.

Microbio-degradative technique has been a useful tool for structural elucidation of fruit tannins and for reduction of astringency in beverages and fruit products. Because of its superior ability to utilize catechin, A. flavus (dicat) was isolated among other soil microorganisms and grown for the production of extracellular, tannin-degrading enzymes. Triton-X-100 was found to be useful in reducing enzyme inactivation by phenolics produced from the degradation of tannins. The dialyzed culture filtrate from A. flavus (dicat) has been shown to remove, in vitro, astringency of cashew apple tannin. After several attempts, the presence of 12 phenolic compounds has been found in cashew apple and three of these compounds were identified. Similar to other fruits, tannin in cashew apple becomes more polymerized in ripening.

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Increasing Exports

Obtusastyrene is active in vitro against Gram positive bacteria, yeasts, and molds. Obtusastyrene is not affected by pH and its minimal inhibitory concentrations, 12-25 ppm for bacteria and 12-100 ppm for fungi, compare well with synthetic preservatives in current use. At 25-50 ppm, obtusastyrene inhibits yeast growth in fruit juices. Thirty obtusastyrene analogues have been synthesized and screened. Initial feeding trials indicate that obtusastyrene has only moderate toxicity to rats. Obtusastyrene and similar compounds are very active in inhibiting germination and outgrowth of spores of Bacillus megaterium. Derivatives of natural phenols have been screened for antimicrobial action, viz., cinnamic acids, umbelliferone (7-hydroxycoumarin), 6,7-dihydroxy and 7,8-dihydroxy-coumarin, 6-hydroxy- and 8-hydroxycoumarin. Some coumarins may be natural plant fungicides. However, they are not active below 500 ppm. 3-Acyl-4-hydroxycoumarins, suggested by the Japanese as food preservatives, are active against bacteria and fungi. 3-Acetyl-4-hydroxycoumarin has been shown to inhibit yeast growth at low concentrations in fruit juice. The activity of 48 compounds vs. the fungi responsible for citrus spoilage has been determined. In vitro tests show 2-cinnamyl-phenol and dihydro-obtusastyrene at 50 ppm. completely inhibit growth of all nine of these organisms.

The search for effects of other agents than radiation (i.e., metals) as synergists and the determination of repair mechanisms is quite important to developing means for reducing dosage requirements for juice sterilization. Research is in progress.

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Microbial Hazards

Methyl bromide has been shown to have antimicrobial properties that completely destroy yeast, mold, and vegetative bacteria in 18 hours, when applied at the rate of 1 lb. per 1000 cu.ft. at 85° F. Spore forming bacteria are more resistant. Temperature increases in the range 60 to 100° F. increase the effectiveness of methyl bromide; altering humidity has less effect on its microbicidal action. Byssochlamys fulva culture was freeze dried and fed to rats. The rats had increased liver weights and cell size as the only abnormalities. Body weight and feed consumption were lower with animals fed up to 8% of the culture in the diet. The liver did not completely return to normal weight after 35 days on a diet without added culture material. Urine ascorbic acid increased with ingestion of the dried culture. More than 90% of ingested byssochlamic acid was recovered unaltered from the feces. Although B. fulva grew in canned juices, byssochlamic acid was not produced.

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Controlling Pollution

A pilot plant size "dry caustic" fruit peeler was built in cooperation with the National Canners Association and the Federal Water Quality Administration. The peeler was designed to reduce water pollution caused by conventional lye peeling of soft fruits. In the "dry caustic" fruit peeler, peeling is accomplished by a bed of spinning soft rubber discs. As lye-treated fruit passes through the peeler, the rubber discs gently wipe loosened peel from the fruit and fling the peel into collectors; the peel is thus kept out of plant effluent waters. The small amount of loosened material remaining on the fruit is removed by a brief water rinsing. The peeler was tested extensively on cling peaches at a local cannery; it successfully peeled cling peach halves diverted from the cannery processing line. The tests show 2-3 tons of peaches per hour can be peeled for each foot of peeler width with a peeling loss equal to that normally sustained by conventional peeling equipment. Compared to a conventional lye peeling operation, water use can be reduced by almost 95% and the total BOD in effluent water by 80-85%. In pilot plant tests, pears and apricots were also successfully peeled. Testing was not as extensive as on peaches but results indicate similar reductions in water usage and BOD probably could be achieved. Exploratory testing on apple peeling is underway.

POTATOES

Problems and Objectives

An historic decline in per capita potato consumption has been reversed by growth of markets for processed products. Consumption has been stabilized at about 110 lbs. since the early 1950's through market growth for processed potatoes. To hold these markets, new and improved products and processes of lower cost must continue to flow from research.

Establishment of large manufacturing plants for potato products has concentrated potato waste which now must be treated to prevent pollution of streams, rivers and lakes. Processes of manufacture must be changed to reduce pollution from potato processing.

Major objectives of the research are to develop and evaluate alternative ways for: (1) Improving color, flavor, and stability of processed potatoes; and (2) Controlling pollution and converting waste products.

Food Uses

By surface freezing raw potato strips and leaching the reducing sugars from the damaged cells with warm water, the surface sugar levels in French fried potato strips can be controlled. Use of this technique may permit lower storage temperatures for tubers, thus reducing respiration and defect losses; eliminate the need for reconditioning at 70° F. after cold storage; and permit the use of varieties that have not been suitable for frying because of their high reducing sugar contents.

A convenient quick-cooking baked potato has been developed. This product is prepared by a processor and can be held in a restaurant refrigerator for 1-2 weeks. It can be prepared for serving in 10 minutes. The finished product is equal or superior to a potato freshly baked in the conventional manner.

Holding frozen French-fried potatoes in the thawed state caused increased moisture loss, increased fat uptake and decreased yield during finish-frying. These effects are not caused by starch retrogradation, but parallel the diffusion of moisture from the center to outer layers of the parfried strips. Calculations based upon size of tissue cells showed that slicing losses due to cut cell components released in the manufacture of potato chips range from 8 to 24 percent of the tuber weight depending on slice thickness. Such losses pose a problem in the reclamation of the protein, starch, and other solids which contribute to water pollution. Estimates place total solids losses for all potato processing at 750 million pounds.

Dry mass and starch content (as % of dry weight) of potato tubers increased whereas levels of sugar, lipid and protein decreased with increasing tuber

maturity. Both growing and mature tubers developed sugar and lost starch during 4° C. but not during 25° C. storage, whereas storage temperature did not greatly influence protein or lipid level or lipid composition. Methods were developed for isolation of membrane fractions from whole tubers and from starch granules in the tubers. Total membrane fractions of whole tubers stored at 4° C. had a higher buoyant density than that from tubers at 25° C. Starch granule membrane from tubers stored at 4° C. had a lower buoyant density than from tubers at 25°. Time but not temperature of storage changed the gel electrophoresis protein pattern of total membrane protein whereas the corresponding pattern of the protein for the starch membrane, different from that of the total membrane, was changed by tuber storage temperature. These correlations suggest that the starch granule membrane may play a role in synthesis, degradation and maintenance of the starch granule and points to further investigation of their structural and enzymatic properties.

The nucleic acid analogues reported last year were further characterized. Some syntheses revised and scaled up, especially the 5-ethyl pyrimidines, because of the finding that ethionine-induced hepatomas contain large amounts of ethylated nucleic acids. The finding that poly-2'-O-methyl cytidylic acid is not an interferon inducer should be helpful in elucidating the mechanism of the anti-viral activity of certain RNA molecules. UV radiation transforms 6-chlorouracil quantitatively to barbituric acid, an example of rarely occurring photodechlorination. Actual isolation of the intermediate (which is a new type of dihydropyrimidine) in the photochemical transformation of 5-ethyl uracil shows that the photoreaction proceeds by intramolecular cyclization. 5'-O-substitution of naphthyl-pyrimidine/purine-5'-phosphates suppresses the ability of these substances to serve as phosphodiesterase substrates but not as RNase substrates. An enzyme activity in wheat seedling has been identified as ribosephosphoryl transferase with no base specificity and requiring a substrate with a free 2'-OH. A radiation induced product of thymine in ethanol, identified as 6-alpha-hydroxyethyl-6-hydro-5-hydroxythymine, reverts to thymine in UV.

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Controlling Pollution

Continued advice and guidance were provided for additional commercial installations of our new dry caustic potato peeling process. The total capacity of all commercial installations now in operation is about 360,000 lbs./hr. The 60,000 lb./hr. dry caustic peeling system in Grand Forks, North Dakota, supported by funds from the Federal Water Quality Administration, is providing data which will subsequently be made available to all potato processors. A FWQA grant to test the commercial feasibility of dry caustic sweet potato peeling has been approved for a cannery in Tabor City, North Carolina. This system should be in operation for the 1971 canning season and favorably affect this rural community by preserving local canning operations that contribute to the general economic strength. Laboratory demonstrations were made on dry caustic peeling of red beets. With minor modifications, the dry caustic peeling process appears applicable to red beets.

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VEGETABLES

Problems and Objectives

Vegetable crops are perishable and seasonal and thus subject to disadvantageous supply and price fluctuations. New products and processed products of improved quality, stability, convenience, nutritive value, safety and cost are needed to sustain domestic and build foreign markets. Processing operations must be changed to cope with the effects of mechanical harvesting and field handling of raw materials. Increased use of agricultural chemicals may require processing changes to mitigate effects of residues. Wastes from processing operations must be handled at reduced costs to prevent polluting soils and bodies of water.

Major objectives of the research are to develop and evaluate alternative ways for: (1) Improving quality and stability of dehydrated vegetables for export. (2) Insuring removal of harmful agricultural residues in processing. (3) Protecting canned low-acid foods and other vegetable products from spoilage bacteria and from microbial contaminants. (4) Improving and developing new and improved foods by evaluating processing characteristics of new varietal selections; devising processes to create convenient, non-flatulent products from dry beans and peas; controlling the consistency of tomato products; and devising better methods for preserving the textural characteristics of frozen vegetables. (5) Alleviating soil and water pollution from vegetable processing wastes.

Processing New Varieties

Green beans subjected to different blanching treatments were frozen in package, IQF by air blast, and by Freon-12 immersion, to determine if different freezing speeds require different blanching treatment. After 6 months of -14° F. storage, no appreciable flavor differences were noted between freezing treatments, and within a blanching treatment; Freon-12 frozen beans had a much superior texture, however. The effect of planting and harvest time upon color of frozen carrots was assayed. Carrots planted in late spring and midsummer were harvested at 90-day intervals, after the carrots had reached pulling size. Carotene and xanthophyll content were measured in Imperator 58, Scarlet Nantes and Royal Chatenay varieties. Royal Chatenay was lowest in carotene, and Imperator highest in xanthophyll. Harvest time influenced xanthophyll content, with a lowering trend. Carotene was higher in raw carrots after 120 days than after 30 days. Both carotene and xanthophyll content dropped slowly during freezing storage at -14° F. Of three new commercial corn varieties tested, Presto gave the best frozen cob corn.

Food Uses

Studies were made of relationships amongst tomato processing variables such as heating, pH level, maceration, pulping, cell damage, blending, and consistency. Typical cold break juices have low consistencies of 20 or 30 sec. flow time, and cell counts of about 7 per field. After blending 2 min., their flow time increased to 60 sec. and cell counts were less than one. Acidification of the original juice to pH 2.75, heating 5 min., cooling, neutralizing and blending greatly reduces the flow time of such juices. When hot break juices having flow time of 50 sec. and whole cell counts of 9 per field, are blended, flow time may increase 1.5 to 3 times and the cell count may decrease to 1 to 4 per field. Such juices when acidified, heated, cooled and blended might have flow times 3 to 4 times greater. When excellent hot break juices, having flow times of more than 100 sec. and cell counts of 15 or higher per field, are blended, the flow times may decrease by one-half. Blending these juices after acidification, heating, neutralization and cooling may increase the flow time to 400 sec. or more. These observations may provide the basis for another processing variation of acid treatment of tomato products for consistency improvement. Preliminary results on drum drying have shown that paste from acid extraction was easier to dry to a better tomato flake than paste obtained from natural pH extraction.

Work has been completed on development of processes for preparing quick-cooking products from dry beans. These include a procedure for home use to improve the cooking rate, texture, and flavor of large Lima beans; processes for preparing a variety of dry, quick-cooking beans including large Limas, blackeye, kidney, pinto, small white, and other common beans whose cooking times have been reduced from 50-75%; a process for preparing frozen, hydrated, quick-cooking bean products which cook in 15 minutes with improved texture, flavor and odor; development of a stable, dry mixture of common salts for use in the home, institutional kitchens or processing plants to produce quick-cooking bean products; a process for preparing hydrated, quick-cooking bean products from dry beans that can be held under refrigeration for 5-8 weeks. Both frozen and dry, quick-cooking, large Lima beans have the same high nutritional value as unprocessed beans. Drying of precooked bean powder on a double drum drier was successfully developed to full-scale commercial production. The material thus prepared is being subjected to extensive market trials.

A method for the quantitative collection and determination of hydrogen gas from the rat shows promise of being a useful assay for estimating the flatulence activity of beans and other food products. The following results have been obtained on bean fractions by human assay: (1) Hot 70% ethanol extraction of defatted dried beans yields material which exhibits somewhat over 50% of the flatulent properties of the control beans. The extract was further separated by treatment with a sulfonated polystyrene ion exchanger. (2) The sugar oligosaccharide fraction and (3) the amino acid-peptide fraction when fed separately at different meals were non-flatulent. When the two were combined and fed together, a flatulence equal to that of the

original bean was observed. These studies, conducted cooperatively with the Department of Nutritional Sciences, U.C., Berkeley, establish that two classes of compounds, when combined, contribute to flatulence and probably at least one additional component contributes since the residue after extraction is still moderately flatulent. γ-Glutamyl-S-methyl-L-cysteine was synthesized for flatulence tests. In the rat assay, this synthetic peptide, S-methyl-L-cysteine, raffinose and stachyose (all bean constituents) each gave hydrogen in excess of the control diet.

A number of pyrazines closely related to the bell pepper compound 2-methoxy-3-iso-butylpyrazine were synthesized. The purified compounds were organoleptically characterized by descriptive analysis and by detection threshold determinations. These data have led to the formulation of mixtures of compounds which show promise as flavor enhancers for a variety of food products. Several components identified in the volatile fraction of potatoes were evaluated for use in improvement of potato products. Methional and 2-methoxy-3-ethylpyrazine were the most useful compounds for enhancing the flavor of potato products. Part of the precursors to onion flavor are present as gamma-glutamyl peptides, and hence unavailable for flavor formation in many food products. Animal kidney and sprouted onions contain enzymes capable of releasing these precursors.

Freezing pieces of vegetable or fruit tissue at very slow rates (less than 1° C./hr.) to temperatures a few degrees below 0° C. appeared to preserve cellular integrity and membrane function so that pigments and electrolyte were retained. Freezing at faster rates, or to lower temperatures, permitted leakage of water-soluble pigments and electrolytes from cells after they were thawed. Resistance to compression was also much greater in tissue ultra-slowly frozen, than in those rapidly frozen. Ultra-slow freezing of whole vegetables and fruits also provided better preservation of some products than did rapid freezing. In preliminary storage experiments, Pippin apples were unaltered after 4 weeks at -4° C. New work will be undertaken to determine the feasibility of using such freezing as a means of preserving foods for a longer time than they could be held in the fresh unfrozen state, and with better quality than that of present unfrozen products.

The study of the effect of blanching conditions and methods on the quality of frozen Brussels sprouts has been continued through a six-months storage period. Chlorophyll, ascorbic acid, pH, total acidity and enzyme activities were determined after three and six months storage. Water was considered the best blanching medium for Brussels sprouts. High temperature (100° C.), short time (1.5 min.) blanches resulted in the highest retention of chlorophyll and ascorbic acid. The location of the sprouts on the plant stem markedly influence dry matter and ascorbic acid contents of the fresh sprouts. Chlorophyll contents of Bordi, Delisa II, Konserwowy, Lincoln, Verdo, and Vitalis pea varieties were compared. Delisa II was used for the study of blanching effects on chlorophyll retention, ascorbic acid retention and enzyme activities through process and 6 months storage. Three minute microwave blanches were less effective against peroxidase than

3 minutes in water at 90° C. or steam for 2.5 minutes. The studies on peas included influence of maturity on dry matter, vitamin C, pH, enzyme activity and chlorophyll content.

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Controlling Pollution

Advantages of field processing of tomatoes were substantiated. California-grown mechanically harvested tomatoes were obtained from a washing station located in the harvest area and processed in a small mobile, field processing unit within six hours of harvest; this prevented the loss of 9% of the ripe tomatoes that occurred when processing was delayed 24 hours. Earlier studies indicate that losses incurred under commercial conditions may greatly exceed 9% because of delay and damage during transportation to processing plants. Inclusion of acid treatment of the hot macerated tomatoes in the process, resulted in an increase of 4.3% solids recovery for a total field processing increase of more than 13%. The juice produced was suitable for bulk transport to a cannery for canning, storage, or concentration, and final processing into sauces, catsup, etc. The increased product yields obtained result in proportionate decreases in solid waste. These wastes can be spread on newly harvested tomato fields, to be disked under with the vines, and cull tomatoes dropped by the harvester. The pulper waste can be dehydrated for animal feed. When the acid treatment is part of the process, the pomace is drier and dehydration can be completed at lower cost. Waste washing and cooling waters can be more readily treated by lagooning, or disposed of via irrigation at a field location, than at a large plant in or near an urban area.

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Microbial Hazards and Residues

Line studies in 15 vegetable freezing plants have shown generally lowering plate counts during the past five years. The 50,000 gram plate count tolerance set by industrial buyers can normally be met by the processors. Negative air pressure conveying (NAPC) of blanched peas, corn, cut beans, has replaced conveyor belts, flumes, bucket elevators, and other processing machinery in many lines. Microbial counts made of samples entering and leaving pneumatic conveyors showed negligible pickup in 54 percent, less than a 5 times increment in 82 percent, and greater than 10 times increment in 7 percent of the tests. Potentially, NAPC can help in keeping microbial contamination down, but must be kept adequately sanitized to do so. Detailed studies of 538 pea, bean, or cob corn samples showed positive presumptive coliform tests in 49 percent. Confirmed coliform tests showed in

37 percent, and Escherichia coli was present in 3 percent of the samples. Aerobacter spp. accounted for most of the coliforms recovered. E. coli was generally present at points following inspection, although in the plant from which the organism was most frequently isolated, an air cleaner was the source. The air cleaners preceded the point of human contact with the product. Plate counts of frozen cooked squash were above 10^6 gram largely due to contamination by static material at transfer points in a five step cooling system. Introduction of a closed system heat exchanger into the system in place of the five step system dropped the product count to less than 50,000/gram.

During the 1970 processing season, 4 lines for processing peas, 3 for beans, 6 for corn, a squash, a diced carrot, and a strawberry line were sampled for microbiological studies. High counts, when found, were at freezing tunnel entrances, locations away from main plant floor. The cooked squash line was remodeled to incorporate rapid cooling of squash puree and elimination of many transfer points where static material could accumulate. Microbial content was then under 50,000 as compared with over a million per gram in product produced in old line. In a French cut bean line, counts jumped from less than 500 in whole beans to 230,000 in sliced beans. Better cooling of beans and more frequent sanitizing of cutters were needed in this situation. Use of NAPC reduced water requirements in plants. High counts were found in samples taken from the discharge end of two NAPC systems. In a plant having high counts in previous years the increase during the 1970 season was controlled by frequent, more thorough sanitizing of NAPC system. Coliforms were not found on hand-picked strawberries from experiment plots, but were found in low numbers on strawberries from a commercial freezing line. The coliform incidence occurred after inspection, slicing and mixing the berries with sugar.

Washing onions before peeling did not reduce the microbial count of the peeled onions. Dipping onion slices in hypochlorite before drying can reduce total count of the dry product without damaging pungency, but browning of the dehydrated onions results. Chlorine dioxide was preferred; dipping solutions of 160 ppm were optimum for total count reduction, whiteness, pungency and odor of the dehydrated product. Heating dry samples at 160° F. for 20 minutes did not affect total counts. The anti-microbial effect of heat was increased by humidification via steam injection but the modified treatment damaged pungency and color. Combined ClO_2 and humid heat treatments resulted in low counts with excellent color and pungency. Dips of 0.3% H_2O_2 were ineffective in reducing total counts. Chlorine dioxide and humid heat treatments aided in destruction of coliform and Salmonella inocula during dehydration. Neither of the latter two treatments had detectable effects on thermophilic spore counts. Studies conducted on potatoes indicated that lye peeling reduces total counts to insignificant numbers. The dicing operation is a possible source of heavy contamination. Drying of dice with dust-contaminated air was found to increase total counts and spore counts.

Obtusastyrene and certain analogs at 10 to 30 ppm inhibit the initial stage of germination of B. megaterium, as well as outgrowth, in a rich medium.

Most growth inhibitors, accepted as (or potential) food additives, do not have both of these effects. This unusual property could be of interest by retarding development of Clostridia in non-sterile products for which safety depends on preferential growth of non-toxic bacteria during incipient spoilage. Proton and calcium ion association constants have been determined for 18 analogs of dipicolinic acid (DPA), a component believed to be involved with calcium in locking the dormant spore into its heat-resistant state. Spore exudate induced by disinfectant chlorine is nearly pure DPA by UV spectrum, and 67% pure CaDPA by weight. All of the histidine, tyrosine, methionine and cystine of the spore protein is destroyed, showing that all of the spore (megaterium) is accessible to chlorine. The hydrogen form is more susceptible than the Ca form of the spore. A high ionic strength generally inhibits spore germination. This is not true of B. macerans germinated with 2-phenylacetamide or pyridoxine, though it is true of other germinants for this spore. It appears that high salt concentrations are more inhibitory of the initial stage of germination, for which alternative paths exist. Benzylpenicillin is the first antibiotic found to germinate spores (macerans).

Six grams of Clostridium botulinum strain 62A spores have been prepared. These spores were found to have somewhat greater than classical heat resistance in their native, untreated form, but have attached sporangia. Extensive application of recommended cleaning methods (lysozyme-trypsin-sonication, high pressure extrusion, various enzymes) has failed to clean these spores of adhering sporangia. Chemical treatment to prepare the hydrogen form of these sporangia-bearing spores reduced their heat resistance. Trials are in progress to maximize heat resistance of the calcium form. Because the adhering non-spore material could magnify the effects of chemical treatment by carrying calcium into the heat challenge environment, attempts to get adequate quantities of clean spores are continuing. Small amounts of clean spores have been obtained recently from single colony isolates grown in modified medium.

Spinach and apricot purees were fortified with radioactive DDT and given simulated commercial heat treatments. After processing, apricots contained 75% unreacted DDT and 16% TDE as a transformation product. Spinach contained 4% DDT, 50% TDE and 2% DDE. Characteristics of the remaining radioactivity in spinach suggest that other transformation products are the result of reactions of DDT and TDE with various free amino acids. The effects of heat processing and subsequent storage on 15 pesticide compounds in spinach and in apricots were determined. The compounds studied were: (organochlorine pesticides, "chlorinated hydrocarbons"), captan, lindane, TDE, thiodan, toxaphene, methoxychlor; (organophosphates) diazinon, guthion, malathion, methyl parathion, trithion; (carbamates) zineb, ziran, maneb, carbaryl. The results indicate that the initial destruction of pesticide residues is due primarily to the length and severity of the heat treatment, together with the degree of acidity of the product. Differences in acidity may affect stability during storage. Organochlorine pesticides were degraded at about the same rate in spinach as in apricots. Organophosphates were

almost completely degraded in both products. The thiocarbamates were almost completely degraded in spinach, but only partially in apricots.

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Increasing Exports

Components of the volatile oil fraction of hops have been separated and identified by capillary gas chromatography (CGC) and mass spectrometry. Fifty components of oils from American and European hop varieties were identified, and the oils classified into different groups according to the presence or absence of key constituents. The classification scheme thus developed provides a method for distinguishing varieties of hops by their volatile constitients. The nonvolatile resin fraction consists mainly of the alpha-acids (humulones) and beta-acids (lupulones), which have closely related structures. The humulones are converted into bittering constituents during the brewing process whereas the lupulones remain unchanged. It has been shown that ultraviolet irradiation of lupulone in methanolic solution results in conversion to desoxyhumulone, from which humulone can be obtained in moderate yield by oxidation. These results indicate a method by which the beta-acids could be converted into alpha-acids, thus resulting in improved utilization of hops or hop extracts during the brewing process. A CGC technique was developed for the analysis of hop resin transformation products present in malt beverages. Although the composition and structures of the hop resin constituents are fairly well elucidated together with their chemical transformation products, the exact nature of the resin-derived components present in malt beverages is not well understood. The CGC technique developed can be combined with mass spectrometry and other physical techniques to identify such constituents completely.

Pilot brews of beers made with European Hallertau species and American Cluster species of hops were extracted with iso-octane to isolate the hop-derived flavoring constituents. Analysis of these constituents by gas-liquid chromatography as their trimethylsilyl ether derivatives showed distinctive and reproducible patterns for each of the hop varieties. Isomerization of commercial extracts of Hallertau and Cluster hops, by boiling in unhopped wort, gives the same patterns on gas-liquid chromatographic analysis as those obtained from the pilot brews prepared with the corresponding hop variety. The method will therefore distinguish between both beers and hop extracts prepared from different hop varieties. The analysis of new hop varieties by the same technique is being used to classify such hops as European or American in character. Pure samples of various

hop alpha-acids, beta-acids and isohumulones have been prepared by isolation and isomerization of hop extracts in order to provide standards for the identification of hop constituents present in beer.

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SAFFLOWER, CASTOR, SESAME, AND OTHER WESTERN OILSEEDS

Problems and Objectives

Cash crops for diversification and rotation programs need to be increased, particularly in cotton-producing areas of the western states. Crops with potential for these programs are safflower, castor and other western oilseeds. New and improved food products, animal feedstuffs, and industrial products from these oilseeds are needed to provide markets for these crops.

Major objectives of the research are to develop and evaluate alternative ways for: (1) Developing improved processes for food products from western oilseeds. (2) Developing industrial products from western seed oils. (3) Developing improved animal feedstuffs from safflower and other western oilseeds. (4) Developing practical methods for production of safe-to-handle deallergenized castor pomace for feed use.

Industrial Uses

An aliphatic diamine 1,12-diaminooctadecane and a diisocyanate 1,12-octadecanediisocyanate were prepared from ricinoleic acid by a series of steps. These involved conversion of ricinoleic acid to 12-ketostearic acid, synthesis of 12-ketostearamide, dehydration to 12-ketostearonitrile and reductive amination to 1,12-diaminooctadecane. This diamine reacts with phosgene to yield the diisocyanate. Thin-layer analytical procedures were used to assess purity of products. Copolymers of acryloxystearoyl chloride with acrylates and methacrylates were prepared by two synthetic methods. The products are polymers with pendant side chains containing reactive groups which bind chemically to wool or other materials having free amine or hydroxyl functions. When applied to wool, the polymers gave shrink-proofing but with good "hand" or feel. An oxo-reaction product of oleic safflower oil prepared by scientists at NMN was converted to 9(10) hydroxymethylstearic acid derivatives and was used in place of castor acids to make acryloxy copolymers as above. These polymers were also applied to wool to impart shrink resistance.

Acrylate esters of fatty acid chlorides were copolymerized with vinyl chloride, producing polymers with pendant side chains having reactive acid chloride groups. A number of polymers were prepared with varying co-monomer ratios for evaluation as building agents to make wool shrink-proof. Use of the very inexpensive co-monomer, vinyl chloride, makes these polymers competitive with ones currently in use for shrink proofing. The polymers allow wool to retain its soft hand because they are internally plasticized.

Di- and tri-functional ricinoleic acid amides prepared from mono- and diethanol and isopropanolamines produced hard urethane elastomers with good properties. Improved softer urethane elastomers were prepared from

mixtures of these amides with castor oil or butanediol diricinoleate. Elastomers from an aliphatic diisocyanate and castor oil were light colored, but weak. Substitution of an amide of ricinoleic acid for castor oil yielded greatly improved elastomers. High density rigid urethane foams from castor oil and other ricinoleate derivatives were formulated.

Series of triacylated and triaroylated monoricinoleins were prepared and evaluated as plasticizers for PVC resins. On balance, the monoricinolein-derived plasticizers were comparable to the established dioctyl phthalate plasticizer. A significant development from this investigation is a novel convenient method for preparing the intermediate monoricinolein by glycerolysis of castor oil utilizing carbon dioxide as a catalyst. Indian Patent No. 71979 was issued for this new process. As a result of the work reported, a plant is being constructed in India for the commercial production of triacylated monoricinoleins for use as PVC plasticizers.

Controlled oxidation of castor oil and methyl ricinoleate with oxygen was accomplished by means of photosensitization, catalysis with metal complexes and use of benzoyl peroxide. Photosensitized oxidation with methylene blue led to formation of a persistent free radical observed by ERS. Product analysis for epoxide, trihydroxy stearate esters and epoxide showed that iron and manganese catalysis produced up to 39.6% trihydroxystearates, while catalysis by cobalt and copper phthalcocyanines gave ca. 15% yields of epoxide.

Addition of Cl_2, Br_2, HCl and HBr to triricinolein was investigated. No useful new techniques or products were found. Attempted addition of HOCl or HOBr to methyl ricinoleate led chiefly to addition of Cl_2 and Br_2. A small amount of solid crystalline product was obtained which appears to be an addition product of HOCl and methyl ricinoleate. Hypohalogenation of triricinolein has been studied, but characterization of the products has not been completed. Esters of triricinolein with chlorendic and tetrachlorophthalic acids were prepared but analyses have not been reported. Bromination with N-bromosuccinimide caused loss of the hydroxyl groups.

Safflower oil was isomerized by three different procedures to give cis, trans-conjugated triglycerides. Maximum conjugation (24.6%) and some elaidinization resulted from heating the oil under nitrogen at 250-260° C. with 5% anthraquinone. The conjugated fatty acids or their methyl esters were further elaidinized and allowed to react with several dienophiles, including acrylic acid, methyl acrylate, methacrylic acid, methyl methacrylate, crotonic acid, cinnamic acid, methyl cinnamate and stryene. Some of the adducts were epoxidized. Studies are continuing on reactions of dienophiles with conjugated safflower triglycerides.

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Feeds

With the aid of a rat bioassay two bitter compounds and a laxative principle were isolated from safflower seed. These three compounds were found to be β-glucosides, and the chemical structures of their aglycones were firmly established. Results from this project should be useful in devising processes to eliminate the undesirable factors from safflower meals for feed and food uses. The color and odor problems in oil from experimental varieties of safflowers were satisfactorily resolved. Modification in processing and refining technique in a pilot plant experiment were successfully employed to eliminate these problems.

Pilot plant scale processes for deallergenizing castor meal have been re-evaluated using the recently developed intradermal guinea pig test (PCA) to estimate residual antigenicity. Commercially feasible processes were developed using steam, ammonia, or lime. Hydroxy fatty acids and ricinine were measured in chickens fed castor meal, castor oil, or synthetic ricinine. At 1% castor oil in the diet, hydroxy fatty acids of chicken adipose tissue amounted to only 0.2%, slightly above the figure for control animals. A 5% castor oil diet led to incorporation of 2.3% hydroxy acid in chicken fat. Eggs from these chickens contained only 0.2% hydroxy fatty acid. Eggs from laying hens fed castor oil showed decreased fertility at the 5% dietary level, but not at the 1% level. Egg production and hatchability were not affected at either level. Synthetic ricinine decreased the growth rate of broiler chicks at levels above 0.04% of the diet. Tissue samples of the chicks indicated that ricinine was not present at detectable levels (1 ppm or higher). Broilers fed an ammonia-treated castor meal ration (24% level) grew as well as those on a soybean meal control. Broilers fed untreated castor meal diets did not do as well as the control group. Tests have been started with dairy cows to study transmission of ricinine, hydroxy fatty acids, ricin and allergens from untreated castor meal based rations.

Numerous samples of processed castor meal have been bioassayed for their ricin content using a mouse test devised for the purpose. Meat and liver samples from steers fed castor meal have also been assayed for evidence of transmission of ricin from the feed into the body tissues; no such evidence was found.

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Food Uses

A new variety of safflower oil, high in oleic acid, was found to be thermally and oxidatively stable and is thus a superior cooking oil; it is now available commercially. Tandem GC-mass spectrometric methods led to identification of components of oxidized fats and oils and of oxidized model compounds. Non-cathartic castor derivatives were found to modify greatly the gelation of starch pastes and flour doughs by viscosity increase in hot pastes. The surface-active properties of the castor derivatives differ from those of current commercial surfactants. Apparatus was designed to monitor oxidation of small amounts of organic materials in a screening program for natural antioxidants. A bidirectional recording gasometer was developed to measure oxidation properties of oils. This instrument is capable of continuously recording very small amounts of gas evolution or gas uptake.

Phosphatides were isolated and analyzed from ordinary and from high-oleic variety safflower seeds. Fatty acid composition of the phosphatides in all cases was similar to that of the triglycerides in the same oil. Two bitter principles of safflower are matairesinol monoglucoside and a steroid glucoside. The position of the glucose in matairesinol glucoside was determined. A method was developed to measure quantitatively isolated *cis* and *trans* double bonds in fatty acid derivatives by Raman spectroscopy. This method promises to be considerably more accurate than the current infrared method.

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EGGS AND TURKEY MEAT

Problems and Objectives

Per capita consumption of eggs has decreased about 10% in the last decade, primarily as a result of decrease in shell egg use. Egg products, eggs removed from the shell and further processed, now constitute about 10% of total production. This phase of the industry has expanded as a result of research designed to provide many high quality egg products which are more convenient to use than shell eggs. It is apparent that the development of versatile egg products could help reverse the downward trend in egg consumption. The unique functional properties for which eggs are valued in food preparation are easily damaged by processing operations such as freezing, drying, heating, and shearing. Research is needed to devise new and improved methods for production of present and new types of egg products. These methods should provide maximum kills of pathogenic microorganisms without significant destruction of the egg's functional properties.

Major objectives of the research are to develop and evaluate alternative ways for: (1) Eliminating processing damage to egg products by developing improved processing methods and new products. (2) Controlling Salmonella in liquid and dried eggs.

Increasingly efficient production of turkey, culminating in vertical integration linking breeder, hatchery, producer and processor, has been largely responsible for the increased production without increase in retail price. The continued low price to the consumer has been achieved without sacrifice in quality or safety of the product, and the per capita consumption of highly nutritious turkey meat has more than doubled in the last 20 years. However, the introduction of new forms of processing and the extension to ready-to-cook and ready-to-serve retail products requires continuing research to assure retention of quality. Of particular importance are the preservation of desirable turkey flavor, prevention of off-flavors, prevention of toughness, and the prevention of health hazards potentially present in such complicated operations.

Major objectives of the research are to develop and evaluate alternative ways for: (1) Controlling Salmonella in turkey meat products. (2) Eliminating aging requirement for frozen turkey. (3) Developing modifications to improve flavor and extend variety of turkey products.

Food Uses

Methods were developed to improve the properties of whole egg preserved by freezing and intended for institutional use to prepare scrambled eggs. Products were developed that possessed, on thawing, the desired smooth appearance and flavor and the low viscosity needed to facilitate mixing

with ingredients used in scrambled eggs. These characteristics were obtained by the combined effects of homogenization and addition of various low levels of liquid skim milk, salt, sugar, or dextrose.

The β-N-acetylglucosaminidase activity of egg white, destroyed at 60° C. at pH 7, was the basis for a possible test for heat treatment of egg white and whole egg. However, the variation in amount of this enzyme in eggs and its instability at pH 9 restricts usefulness of this test.

Emulsifying characteristics were determined for light and dark chicken and turkey meat, their constituent protein fractions, and yield of deboned comminuted meat prepared with Paoli and Beehive machines from chicken backs and necks and turkey frames. Optimum proportions of constituents, chopping temperatures and chopping times were established. Optimum values were determined for pH in relation to emulsifying capacity, cooked stability, and tensile strength. The effect of salt concentration and salt pre-blending and holding on performance were studied. Of the various protein components of poultry meat, myosin had the highest emulsifying capacity, followed by actomyosin. Sarcoplasmic proteins had high emulsifying capacity at pH 6.0, but produced very thin emulsions compared to those from myosin or actomyosin. Added soy protein increased emulsion stability and tensile strength of cooked emulsions. Fresh deboned turkey meat added at the 15% level to frankfurter formulations gave products that could not be distinguished from samples prepared without turkey meat. The results of this contract research show that chicken and turkey byproducts can be used readily in sausage-type products.

Kinetic and physicochemical studies indicate that natural thinning of egg white is due to alkaline hydrolysis of ovomucin disulfide bonds. Two egg white globulins were purified and characterized: δ_2-macroglobulin and ovoinhibitor; the latter is a trypsin and chymotrypsin inhibitor, and a natural defense of the egg against microbial invasion. The nature, strength, and stoichiometry of the binding of ovoinhibitor to trypsin were determined. An assay for proteolytic enzymes in the presence of inhibitors was devised. A simple procedure for purifying the trypsin inhibitor, ovomucoid, was devised. Kinetics of hydrolysis of the disulfide bonds of ovomucoid by alkali were determined. Changes in UV absorption of proteins near 230 mμ on denaturation were shown to be due to perturbations of aromatic amino acid residues. An ultrafilter for concentration of high molecular weight solutes and a constant head device for column chromatography were devised. Sugar nucleotides were found in egg white and identified.

Ovomucin, the structural protein of egg white, was purified and characterized. A method was devised to free it of lysozyme. A modification of the ovomucin preparation procedure was devised in which the ovomucin was solubilized by addition of 4 molar urea. Solubility is retained when urea is subsequently removed by dialysis. Addition of lysozyme to ovomucin produces a marked increase in turbidity after the amount of lysozyme added exceeds a certain value. The amount of lysozyme required to produce turbidity was not a function of temperature between 0° and 40° C. The

rate of turbidity formation was a function of pH. Ionic strength of 0.5 or above prevented formation of turbidity, as did removal of the positive groups of lysozyme by acetylation. Insoluble lysozyme-ovomucin complex could be dissolved at high salt concentration and the components separated by gel filtration to determine the amount of lysozyme bound to ovomucin. Since the ovomucin-lysozme complex is altered during pasteurization, causing variations in whipping qualities, application of these results may help to improve the quality of pasteurized egg white.

Chicken breast meat is tender when cooked immediately post mortem, becomes minimally tender in 3-4 hours, then increasingly tender until 9 hours aging. Decreasing extractability of myosin, increasing formation of actomyosin and increasing ease of fragmentation of myofibrils parallel changes in tenderness. Glycolysis-inhibiting agents markedly alter these patterns. Actin extractability increases with time until rigor mortis is established, after which no changes occur. A method was developed for the measurement of the contribution of connective tissue to meat texture. No changes with time post mortem were observed in connective tissue content, kind and number of C-terminal amino acids of actin, or sulfhydryl content. The autolytic and catheptic activities of chicken muscle tissues have been characterized because these enzymes may play a role in tenderization. Comparisons were made of myosins from white and red muscle of chicken and rabbit.

Cooked chicken aroma was separated into fractions by passing nitrogen gas, laden with the freshly formed aroma, through solid absorbents or solutions of metal salts. When hydrogen sulfide was removed by any of a variety of heavy metal salts, a completely foreign, disagreeable aroma remained, indicating the blending or masking effect of hydrogen sulfide. When hydrogen sulfide and other components were removed by magnesium oxide, an ammoniacal odor, characteristic of ammonia or aliphatic amines, was exposed. Identification was made of 62 of the approximately 225 compounds evident on the chromatogram of the volatiles from boiling chicken. It was confirmed that cooked chicken flavor does not originate in poultry fat but, rather, that it forms from lean meat and is absorbed in the fat. Hydrogen sulfide not only contributes directly to poultry aroma, but reacts with carbonyls in fat to yield odorous substances that may contribute to typical poultry aroma. A method was developed for determining sulfur in poultry fat, in the range 0 to 10 µg. per gram of fat. Off-flavors, as distinguished from typical flavor, are associated with the fat. Fishiness off-flavor, encountered recently, appears to be due, at least in part, to preservation by ethoxyquin of fishiness-producing components in the residual fat in fish meals.

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Microbial Hazards

It was shown that sub-atmospheric steam at normal scalding temperatures and times can be used to replace the common bath water scald tank on broilers, fowl and turkeys. A steam temperature of 124° F. for 2 minutes loosens broiler feathers as well as tank scalding at 128° F. for 2 minutes.

The air sacs of steam-scalded broilers contained very few bacteria compared with those of tank-scalded birds (more than 1,000-fold difference). The method is easy to control as far as variations in temperature are concerned and provides a uniform scald that yields very little abrasion of the cuticle when birds are picked on commercial processing lines. Possibilities for developing efficient and economical equipment to operate at commercial line speeds are being determined.

Small-scale continuous pasteurizers are especially subject to laminar flow causing the product to receive non-uniform treatment. Therefore, a laboratory scale, slug-flow, continuous pasteurizer was constructed to obtain uniformly pasteurized products in sufficient quantity to conduct functional property tests. The approximate limits of pasteurization time and temperature that various egg products will tolerate without important changes in their functional performance were determined in this apparatus. The limiting conditions provide a wide margin of safety with respect to Salmonella destruction. The laboratory-pasteurizer was also used to confirm that a lower pasteurization temperature is permissible for egg white adjusted to pH 9.5 and supplemented with sodium polyphosphate. The slug-flow pasteurizer and commercial-type equipment correlate well with regard to microbiological destruction and egg product performance. Therefore, the laboratory pasteurizer can be used to test new proposed pasteurizing procedures.

Pseudomonads are gram-negative bacteria that produce "green rots" in shell eggs. All 40 strains tested were found to synthesize and excrete iron transport compounds (ITC) belonging to the hydroxamate family. These compounds reverse the bacteriostatic action of conalbumin, the main defense mechanism of shell eggs against gram-negative bacteria. Milligram amounts were isolated, but only microgram quantities of the preparations were required to promote the growth of Pseudomonads in egg white or stimulate the multiplication of gram-negative bacteria of other genera. Thus the importance of iron transport compounds in the bacterial spoilage of shell eggs is clearly demonstrated. The biosynthesis of ITC by a particular strain of Pseudomonas was critically affected by temperature: positive at 25° C. and absent at 28° C. Growth of this organism in a succinate salts medium, although luxurious at 25° and 28° C., does not occur at 31° C., even in the presence of 10 p.p.m. Fe. The inability of the bacterium to multiply at 31° C. is due to its inability to synthesize ITC at this temperature, since supplementation with microgram amounts of these compounds promoted growth at 31° C.

The genus Salmonella is classified in part by failure to produce acetoin under conditions used for the Voges-Proskauer test. We have shown that all strains tested (more than 40) do so under somewhat different nutritional and environmental conditions.

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